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SODIUM SULPHATE: ITS SOURCES AND USES

BY

ROGER C. WELLS







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CONTENTS.

Introduction	
Demand	
Forms	
Uses	
Mineralogy of principal compounds of sodium sulphate	
Mirabilite	
Thenardite	
Aphthitalite	
Bloedite	
Glauberite	
Hanksite	
Miscellaneous minerals	
Solubility of sodium sulphate	
Transition temperature of sodium sulphate	
Reciprocal salt pair, sodium sulphate and potassium chloride	
Relations at 0° C	
Relations at 25° C	
Relations at 50° C	
Relations at 75° and 100° C	
Salt cake	
Glauber's salt	
Niter cake	-
Natural sodium sulphate	
Origin	
Deposits	
Arizona	
California	
Colorado	
· Idaho	
Nevada	
New Mexico	
Oregon	
Texas	
Utah	
Washington	
Wyoming	
Canada	
Mexico	
South America	
Africa	
Asia	
Europe	
Sulphate process of making wood pulp	
Sodium sulphide	

Prospe Survey	ctin ' pu'	dium sulphate in glass making g permits and mining leases blications relating to sodium sulphate	Page 30 30 40 41
		ILLUSTRATIONS.	
			Page
FIGURE	1.	Mirabilite	
	2.	Thenardite	
	3.	Glauberite	
		Hanksite	
		Solubility of sodium sulphate in water	
		Equilibrium diagram of certain salts at 0° C	
		Equilibrium diagram of certain salts at 25° C	;
		Equilibrium diagram of certain salts at 50° C	10
,		Equilibrium diagram of certain salts at 75° C	1
		Equilibrium diagram of certain salts at 100° C	1:
		Prices of salt cake per ton in the New York chemical market_	1
		Map showing alkali flat in Dona Ana County, N. Mex.	2
	13.	Schematic outline of the sulphate process of making wood	

pulp_____

34

SODIUM SULPHATE: ITS SOURCES AND USES.

By Roger C. Wells.

INTRODUCTION.

Demand.—The recent demand for sodium sulphate for export has greatly stimulated the search for deposits of the natural salt in several of the Western States, and so many requests for information about the sources and uses of sodium sulphate have come to the United States Geological Survey that it has appeared desirable to publish a brief summary of the information available. The foreign demand has come chiefly from Sweden and Canada, where sodium sulphate is used in the sulphate process of making wood pulp that goes into the manufacture of kraft paper. The normal source of sodium sulphate for Sweden was Germany, but since the war the supply from that source has not been adequate. The domestic demand in the United States has also tended to increase, whereas the production of calcined salt cake, the principal form in which sodium sulphate enters trade, has tended to decrease, as will be explained more fully later.

Forms.—Sodium sulphate is handled in trade in three forms—salt cake, Glauber's salt, and niter cake. It occurs in nature as Glauber's salt, which is known mineralogically as mirabilite, and as the anhydrous sulphate, thenardite, and it is a constituent of a number of compound minerals, such as glauberite, vanthoffite, bloedite, and aphthitalite, and of the waters of many natural brines and playa lakes.

In areas where rainfall is scanty sodium sulphate is termed white alkali in contrast to sodium carbonate, which is termed black alkali on account of its corrosive action on vegetation.

Uses.—In the form of salt cake sodium sulphate is used in making wood pulp by the sulphate process, plate glass, window glass, and bottles, water glass, sodium sulphide, and precipitated barium sulphate (blanc fixe). One of the early patents for ore flotation by the Delprat process was based on the use of acid and salt cake.

Glauber's salt is used in dyeing, in tanning, and medicinally, especially for the treatment of cattle as a constituent of so-called stock feeds.

Niter cake is used as a substitute for sulphuric acid for many purposes, as in metal pickling, in absorbing ammonia, and in making fertilizers.

Some details about the use of sodium sulphate in making glass, sodium sulphide, and wood pulp are given on pages 33-36.

MINERALOGY OF PRINCIPAL COMPOUNDS OF SODIUM SULPHATE.¹

Mirabilite.—Hydrated sodium sulphate, Na₂SO₄.10H₂O. Composition, sodium sulphate (Na₂SO₄), 44.1 per cent; water (H₂O), 55.9 per cent. Crystals monoclinic: Axial ratio, a:b:c=1.1158:1:1.2372; $\beta=72^{\circ}$ 15'= (001) \wedge (100), (100) \wedge (110)=46° 44', (001) \wedge (101)=57° 55', (001) \wedge (011)=49° 41'; common forms, a (100), b (010), c (001), m (110), r (101): habit, long prismatic, almost needlelike, elongated parallel to b axis, also short, stout prismatic, elongated parallel to vertical axis c (somewhat resembling borax). Cleavage, a

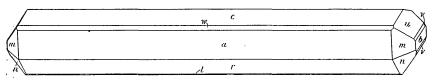


FIGURE 1.-Mirabilite.

perfect. Hardness, 1.5–2. Specific gravity, 1.48. Colorless transparent to white opaque. Luster, vitreous. Indices of refraction: $\alpha=1.394$; $\beta=1.396$; $\gamma=1.398$. Optically negative. Axial plane and acute bisectrix normal to b (010). Axial angle very large, cross dispersion very strong, no extinction in white light. Taste slightly bitter. Very readily soluble in water.

The long prismatic crystals of mirabilite shown in Figure 1 are very characteristic; they readily effloresce in dry air, losing their water and falling to a white powder.

Thenardite.—Anhydrous sodium sulphate, Na₂SO₄. Composition, sodium oxide (Na₂O), 56.3 per cent; sulphur trioxide (SO₃), 43.7 per cent. Crystals orthorhombic: Axial ratio, °a:b:c=0.5976: 1:1.2524; (100) \wedge (110) = 30° 52′, (001) \wedge (101) = 64° 30′, (001) \wedge (011) = 51° 24′; common forms, c (001), a (110), m (110), o (111), t (106). Twinning planes (101) and (011); habit, in pyramidal and tabular crystals, commonly in crossed twins. Cleavage, basal distinct. Hardness, 2.5. Specific gravity, 2.68. Color, white, gray, or brownish. Transparent to translucent. Indices of refraction: $\alpha = 1.464$; $\beta = 1.474$; $\gamma = 1.485$. Optically positive. Axial

¹ Prepared with the assistance of W. T Schaller, of the United States Geological Survey. Indices of refraction by E. S. Larsen, also of the Geological Survey.

plane parallel to (001); acute bisectrix normal to b (010). Axial angle nearly 90°, $\rho > V$ perceptible. Very soluble in water. Taste faintly saline.

The twin crystals (Fig. 2), are very characteristic, but the mineral also occurs massive without any distinct individual crystal form.

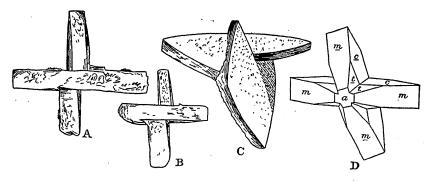


FIGURE 2.-Thenardite.

Aphthitalite.—Double sulphate of sodium and potassium, $(Na,K)_2SO_4$. Composition, sodium sulphate (Na_2SO_4) , generally 21-38 per cent; potassium sulphate (K_2SO_4) , 62-78 per cent. Crystals hexagonal rhombohedral: Axial ratio c=1.2839; $(0001) \land (10\overline{1}1)=56^{\circ}\ 00'$, $(0001) \land (10\overline{1}2)=36^{\circ}\ 33'$; common forms $c\ (0001)$, $m\ (10\overline{1}0)$, $e\ (10\overline{1}2)$; habit rhombohedral, commonly thin tabular, also in pseudohexagonal repeated twins. Cleavage, $m\ distinct$. Hardness, 3-3.5. Specific gravity, 2.64. Colorless to white, tinged with blue or green. Luster, vitreous, inclining to resinous. Transparent to opaque. Optically uniaxial positive. Indices of refraction, slightly variable with composition $\omega=1.49$; $\epsilon=1.50$. Soluble in water. Taste, saline, bitter, and disagreeable.

Bloedite.—Hydrated double sulphate of sodium and magnesium, Na₂SO₄.MgSO₄.4H₂O. Composition, sodium sulphate (Na₂SO₄), 42.5 per cent; magnesium sulphate (MgSO₄), 36.0 per cent; water (H₂O), 21.5 per cent. Crystals monoclinic: Axial ratio, a:b:c=1.3494:1:0.6705; $\beta=79^{\circ}$ 22'=(001) \wedge (100), (100) \wedge (110)=52° 59', (001) \wedge (101)=28° 16', (001) \wedge (011)=33° 23'; common forms, a (100), b (010), c (001), m (110), b (011), p (111), q (201); habit, short prismatic to thick tabular parallel to c (001). Cleavage, none. Hardness, 2.5. Specific gravity, 2.25. Colorless transparent to black, green, red, and other colors due to impurities. Luster, vitreous; clear, glassy colorless fragments resemble quartz fragments in appearance. Indices of refraction: $\alpha=1.486$, $\beta=1.488$, $\gamma=1.489$. Optically negative. Axial plane parallel to b (010). Axial angle, $2V=71^{\circ}$; ρ greater than violet, strong.

Some crystals are covered with a large number of crystal faces, and single crystals weighing a pound are occasionally found. The mineral also occurs granular, massive, and some varieties show a fibrous character.

Glauberite.—Anhydrous sodium-calcium sulphate, Na₂SO₄.CaSO₄. Composition, sodium sulphate (Na₂SO₄), 51.1 per cent; calcium sulphate (CaSO₄), 48.9 per cent. Crystals monoclinic: Axial ratio, a:b:c=1.2200:1:1.0275; $\beta=67^{\circ}49'=(001) \land (100)$; $(100) \land (110)=48^{\circ}29'$; $(001) \land (101)=30^{\circ}37'$; $(001) \land (011)=43^{\circ}34'$; $(001) \land (110)=75^{\circ}30'$; $(001) \land (111)=43^{\circ}02'$; common forms, a (100), c (001), m (110), s (111); habit, short and long prismatic by extension of pyramidal faces s (111), also thin tabular parallel to the base c (001), faces commonly striated parallel to intersection of c (001), s (111), and m (110). Cleavage, basal perfect. Fracture, conchoidal, Hardness, 2.5–3. Specific gravity, 2.7–2.85. Colorless, white, gray,

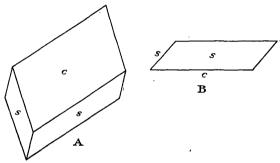


FIGURE 3.-Glauberite.

pale yellow, or red. Streak, white. Luster, vitreous. Transparent to translucent. Indices of refraction: $\alpha = 1.515$, $\beta = 1.532$, $\gamma = 1.536$, Optically negative. Axial plane normal to (010) but varying with temperature. Axial angle very small but changing rapidly with slight change in temperature.

Glauberite whitens in pure water, owing to the solution of sodium sulphate and deposition of gypsum. Crystals have been noted in Saline Valley and Death Valley, Calif.² (See Fig. 3.)

Hanksite.—A triple salt, $9\text{Na}_2\text{SO}_4.2\text{Na}_2\text{CO}_3$.KCl. Composition, sodium sulphate (Na_2SO_4) , 81.7 per cent; sodium carbonate (Na_2CO_3) , 13.5 per cent; potassium chloride (KCl), 4.8 per cent. Crystals hexagonal: Axial ratio, c=1.0140; $(0001) \land (10\overline{1}1)=49^\circ$ 30'; common forms, c (0001), m (10 $\overline{1}0$), o (10 $\overline{1}1$), s (20 $\overline{2}1$); habit, tabular, prismatic and pyramidal, resembling crystals of quartz. Cleavage, basal distinct. Hardness, 3-3.5. Specific gravity, 2.56. Colorless to white, gray, yellow, often clouded by impurities. Luster, vitreous. Transparent to opaque. Optically uni-

² Gale, H. S., Salines in southeastern California: U. S. Geol. Survey Bull. 580, p. 303, 1915.

axial, negative. Indices of refraction: $\omega = 1.481$, $\epsilon = 1.461$. Readily soluble in water, effervescing with acids. (See Fig. 4.)

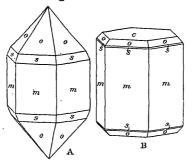


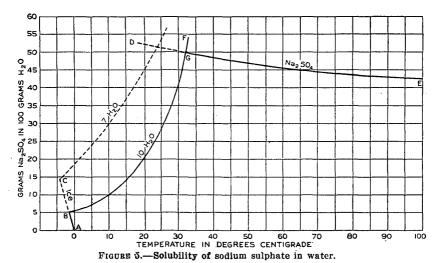
FIGURE 4.-Hanksite.

Miscellaneous minerals.—The following minerals contain sodium sulphate but not enough to be of any value at present:

Ferronatrite	3Na ₂ SO ₄ .Fe ₂ (SO ₄) ₃ .6H ₂ O.
Loeweite	\dots 2Na ₂ SO ₄ .2MgSO ₄ .5H ₂ O.
Mendozite	Na_2SO_4 . $Al_2(SO_4)_3$. $24H_2O$.
	Na_2SO_4 . $Cu_4(OH)_2(SO_4)_2$. $2H_2O$.
Natrojarosite	Na ₂ SO ₄ .2Fe ₂ (OH) ₄ SO ₄ .
	$2\text{Na}_{2}\text{SO}_{4}$.Fe ₂ (OH) ₂ (SO ₄) ₂ .6H ₂ O.
Sulphohalite	2Na ₂ SO ₄ .NaCl.NaF (slightly soluble).
Tamarugite	

SOLUBILITY OF SODIUM SULPHATE.

The solubility of sodium sulphate is of interest geologically in connection with the natural occurrence of the minerals and waters



that contain it and also technically in reference to methods of extraction and separation from the mixtures in which it occurs.

The solubility curve of pure sodium sulphate, based on the data given in Table 1, is shown in Figure 5.

Table 1.—Solubility of sodium sulphate in water.

Temperature (°C.).	Solid phase.	Grams anhy- drous Na ₂ SO ₄ to 100 grams H ₂ O.	Authority.
- 1.2 - 3.55 0	Ice and Glauber's salt. Ice and Na ₂ SO ₄ .7H ₂ O Glauber's salt.	14.5 5.0	De Coppet, Zeitschr. physikal. Chemie, vol. 22, p. 239, 1897.
10 15 20 25 30 0 10 20 26 18 20 24, 4 25	d0 d0 d0 d0 d0 d0 d0 d0	13. 2 19. 4 28. 0 19. 6 30. 5 44. 7 55. 3 52. 8 51. 8 50. 4	Loewel, Annales chimie et phys., 3d ser., vol. 49, p. 50, 1857.
32. 383	Glauber's salt and Na ₂ SO ₄		Richards and Wells, Zeitschr. physikal Chemie, vol. 43, p. 465, 1903.
35 40 50 60 70 80 90	Na ₂ SO ₄	48. 2 46. 8 45. 5 44. 5	Gay-Lussac, Annales chimie et phys., vol. 11, p. 312, 1819.

In Figure 5 the line AB shows the depression of the freezing point of pure water on the introduction of sodium sulphate. At the point B the solution becomes saturated with the decahydrate, mirabilite, or Glauber's salt, the solubility curve of which is the line BF. If by chance the solution is not inoculated with the decahydrate the freezing point may fall to the point C, which is the intersection point of the solubility curve of the heptahydrate, shown by the dotted line. The heptahydrate is unstable in the presence of the decahydrate.

TRANSITION TEMPERATURE OF SODIUM SULPHATE.

The point G, Figure 5, which is the intersection point of the solubility curve of the decahydrate and the anhydrous salt, is also the transition point of the decahydrate into anhydrous salt and its saturated solution. This transition, which is a chemical change accompanied by an absorption of heat, takes place at 32.38° C. if the salts involved are pure; but the transition temperature, or temperature of equilibrium of the two phases, is lowered by the presence of impurities, and when the solution is saturated with other salts it is lowered very considerably, as shown in Table 2.

7.,11

Table 2.—Transition temperature of sodium sulphate with and without the presence of certain other salts.

Solid phase.	Transition tempera- ture (°C.).	Authority.
Na ₂ SO ₄ .10H ₂ O, Na ₂ SO ₄ . Na ₂ SO ₄ .10H ₂ O, Na ₂ SO ₄ , aphthitalite Na ₂ SO ₄ .10H ₂ O, Na ₂ SO ₄ , NaCl. Na ₂ SO ₄ .10H ₂ O, Na ₂ SO ₄ , NaCl, aphthitalite.	32, 383 30, 1 17, 9 16, 3	Richards and Wells. Myerhoffer and Saunders. Do. Do.

RECIPROCAL SALT PAIR, SODIUM SULPHATE AND POTASSIUM CHLORIDE.

The above figures show how greatly the solubility of a single salt may be influenced by the presence of other salts. To show the many possible relations in such associations, physical chemists are accustomed to employ diagrams that reveal at a glance the fields of saturation of the several salts in mixtures. For the sake of simplicity, however, such diagrams are generally restricted to show the relations of not more than four components at one time. Among such combinations the so-called reciprocal salt pairs have been extensively investigated; these constitute a special class in which the composition of the solutions can be expressed in terms of three salts. One of the most thoroughly studied reciprocal salt pairs is that of sodium sulphate and potassium chloride, which will be discussed here in detail, as studied by Myerhoffer and Saunders and more recently by W. C. Blasdale.

The two salts mentioned may undergo a double decomposition, thus,

Besides these four simple salts there are the hydrate, Glauber's salt, and the double salt, (Na, K)₂SO₄, aphthitalite, to be considered. As will be seen from the tables the composition of any solution containing these salts can be expressed in terms of three salts, for the quantity of the fourth salt can always be expressed as equal to two of the others minus the third; thus for NaCl,

$$NaCl=Na_2SO_4+2KCl-K_2SO_4$$

Similar data for solutions saturated with bloedite, glauberite, kieserite, polyhalite, and other salts are to be found in the papers of Van't Hoff and his collaborators. The best collection of data is "Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen," edited by Precht and Cohen, published at Leipzig in 1912.

4 Jour. Ind. Eng. Chemistry, vol. 10, p. 344, 1918.

³ Zeitschr. physikal. Chemie, vol. 28, p. 453; vol. 31, p. 370, 1899.

Relations at 0° C.—The composition of solutions saturated with one or more of the salts involved at 0° C. is given in Table 3, first as grams per 100 grams of water, and second as gram-molecules, or

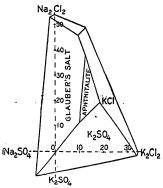


FIGURE 6.—Equilibrium diagram of certain salts at 0° C. Figures indicate mols per 1,000 mols of water.

mols, per 1,000 mols of water. The second form of expression is necessary in constructing the diagram, Figure 6. In constructing this diagram, in which the concentration of the salts is plotted in the respective directions, when the solution is stated to contain three salts, the figures for the solubility of one of the salts must necessarily be subtracted; to this extent the representation is conventional, and the solubility of single salts in the mixtures can not be read directly from the diagram unless the total number of mols present is known.

If desired, however, the totals may be represented by perpendiculars to the plane of the diagram, giving a solid model from which the solubilities of the single salts can be derived for all possible mixtures.

Table 3.—Composition of solutions saturated with certain salts at 0° C.

In grams per 100 grams of water.

	Saturated with—	NaCl	KCI	Na ₂ SO ₄	K₂SO₄	Specific gravity f solution.
A ₁ B ₁	Na ₂ SO ₄ K ₂ SO ₄			4. 62	7. 23	1. 043 1. 063
$\mathbf{D_i}$	KCl. NaCl.	34.95				1.153 1.206
G_1	Glauber's salt and K ₂ SO ₄ K ₂ SO ₄ and KCl		27.88		9.00 1.21	1.118
HI LI LI NI OI PI	NaCl and KCl. NaCl and Glauber's salt. KsO4, KCl, aphthitalite. NaCl, Glauber's salt, KCl. KCl, Glauber's salt, Kptl. KCl, Glauber's salt, aphthitalite. KsO4, Glauber's salt, aphthitalite.	34. 48 13. 38 32. 08 27. 07	10. 55 17. 78 7. 81 10. 06 13. 24	1. 70 2. 78 3. 62		1, 185 1, 188 1, 240 1, 232

In mols per 1,000 mols of water.

	Saturated with—	Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K2SO4	Sum.
A _l	Na ₂ SO ₄			5. 85	7, 47	5. 85 7. 47
Č,	KCl. NaCl.	·	34. 05	. .		34. 05 53. 84
ABCDEGHLLNOP	Glauber's salt and K ₂ SO ₄			7.99	9.30	17. 29 34. 91
Ĥ, L	NaCl and KCl NaCl and Glauber's salt	48.58				61, 33 55, 60
$\frac{\mathbf{L_1}}{\mathbf{N_1}}$	K ₂ SO ₄ , KCl, aphthitalite	19. 41 49. 44	21. 48 9. 43			43. 76 62. 62
O ₁ P ₁	KCl, Glauber's salt, aphthitalite K ₂ SO ₄ , Glauber's salt, aphthitalite	41, 71 11, 50	12. 15 16. 00	6.0	3.35	57. 21 33. 50

The striking characteristic of Figure 6 is the great extent of the field of saturation of Glauber's salt, as compared with the small

extent of the field of saturation of aphthitalite (Na, K)₂SO₄. Thenardite (Na₂SO₄) has no field of saturation on this diagram, and the sodium chloride field is not large. These facts accord with expectations based on Figure 5 and show that the best way to separate sodium sulphate from certain mixtures is to chill the solutions and remove the Glauber's salt. The separation of Glauber's salt in cold weather from the water of saline lakes and ponds in many of the

Western States has frequently been observed. In fact, its deposition from even the water of the Great Salt Lake, which at ordinary temperature is far from saturated with this salt, has long been known, and experiments by the writer have shown that this separation begins in the lake water at 1° C., just above the freezing

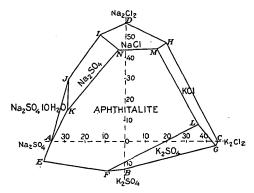


FIGURE 7.—Equilibrium diagram of certain salts at 25°C. Figures indicate mols per 1,000 mols of water.

point of pure water. The temperature at which the separation of potassium sulphate begins was not determined.

Relations at 25° C.—The solubility data for a temperature of 25° C. are given in Table 4, and the phase diagram in Figure 7. It will be seen from the diagram that the field of saturation of Glauber's salt has become very small, and the existence of this phase can not be expected at much over 25°. On the other hand, the thenardite field appears, the fields of sodium chloride and aphthitalite are larger than at 0°, and that of potassium sulphate is much smaller.

Table 4.—Composition of solutions saturated with certain salts at 25° C.

In grams per 100 grams of water.

	Saturated with—	NaCl	KCl	Na ₂ SO ₄	K2SO4	Specific gravity of solution.
A ₂ B ₂ C ₂ D ₂ E ₂ F ₂ G ₂ H ₂ J ₂ K ₂ L ₃ N ₂	Na ₂ SO ₄ . K ₂ SO ₄ . K ₂ SO ₄ . KCl. NaCl. Na ₂ SO ₄ and aphthitalite. K ₂ SO ₄ and aphthitalite. K ₂ SO ₄ and KCl. KCl and NaCl. NaCl and NaSO ₄ . Na ₂ SO ₄ and Glauber's salt. Y. Na ₂ SO ₄ and Glauber's salt. KCl, K ₂ SO ₄ , aphthitalite. KCl, NaCl, aphthitalite. NaCl, Na ₂ SO ₄ , aphthitalite.	29. 88 32. 16 18. 82 14. 28 6. 78 27. 96	36, 96 36, 63 16, 28 29, 38 16, 37	30. 97 6. 69 9. 81 21. 68 22. 28	9. 31 13. 24 1. 53	1. 212 1. 088 1. 187 1. 199 1. 282 1. 149 1. 239 1. 243 1. 273 1. 200 1. 250

Table 4.—Composition of solutions saturated with certain salts at 25° C.—Con.

In mols per 1,000 mols of water.

Saturated w	ith— Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K2SO4	Sum.
B ₂ K ₂ SO ₄					35, 41 12, 46 44, 62
$egin{array}{lll} D_2 & NaCl. & \\ E_2 & Na_2SO_4 \ and \ aphthitalite. & \\ F_2 & K_2SO_4 \ and \ aphthitalite. & \\ \end{array}$	54, 90 46, 04 49, 56 29, 00 hthitalite 21, 92 10, 45 43, 08	44. 11 19. 66 	39. 27 8. 48 12. 44 27. 5 28. 25	9. 63 13. 69 1. 50 	44, 62 54, 90 48, 90 22, 17 45, 61 65, 70 62, 00 56, 50 57, 74 48, 24 67, 31 68, 00

Relations at 50° C.—From the data given in Table 5 and the diagram of Figure 8 it is seen that at 50° Glauber's salt does not exist, most of its area being in the thenardite field.

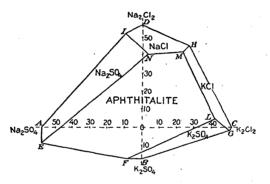


FIGURE 8.—Equilibrium diagram of certain salts at 50° C. Figures indicate mols per 1,000 mols of water.

Table 5.—Composition of solutions saturated with certain salts at 50° C.

In grams per 100 grams of water.

-	Saturated with—	NaCl	KCl	Na ₂ SO ₄	K2SO4	Specific gravity of solution.
As Ba	Na ₂ SO ₄			44. 84	17.09	1.301 1.110
Cs	KCl				1	1. 198 1. 188
$\mathbf{D_8}$ $\mathbf{E_8}$	NaCl Na ₂ SO ₄ and aphthitalite			45.73	9.40	1.351
F ₈ G ₈	K ₂ SO ₄ and aphthitalite KCl and K ₂ SO ₄		42. 24	6.79	17.36 1.84	1.307 1.212
H ₈ I ₈	KCl and NaCl NaCl and Na ₂ SO ₄	29. 09 33. 70	22.03	7.34		1. 246 1. 223
Ls	K ₂ SO ₄ , KCl, aphthitalite	4.68	35.06 22.43	3. 15	2.59	1. 203 1. 254
M_8 N_8	NaCl, Naci, aphthitalite		14.58	11.74		1. 248

Table 5.—Composition of solutions saturated with certain salts at 50° C.—Con.

In mols per 1,000 mols of water.

	Saturated with—	Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K2804	Sum.
As Bs	Na ₂ SO ₄			56. 86	17.60	56.8
Cs Ds	KCl. NaCl.		52.10			52.10 56.2
Es Fs	Na ₂ SO ₄ and aphthitalite. K ₂ SO ₄ and aphthitalite.		. <i></i>	58.00	9.72 17.95	67. 7: 26. 5
Gs Hs	KCl and K ₂ SO ₄ KCl and NaCl	44.82	51.03 26.61			52. 9 71. 4
Is Ls	NaCl and Na ₂ SO ₄	51. 93 7. 21				61. 1 52. 2
Ms Ns	KCl, NaCl, aphthitalite	41.36 40.15	27. 01 14. 58			72. 3 66. 4

Relations at 75° and 100° C.—The diagrams for temperatures of 75° and 100° C. are very similar, but the increasing solubility of

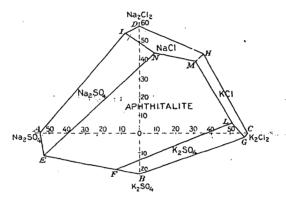


FIGURE 9.—Equilibrium diagram of certain salts at 75° C. Figures indicate mols per 1,000 mols of water.

the potassium salts is noteworthy. The data are given in Tables 6 and 7 and the diagrams in Figures 9 and 10.

Table 6.—Composition of solutions saturated with certain salts at 75° C.

In grams per 100 grams of water.

	Saturated with—	NaCl	KCI	Na ₂ SO ₄	K₂SO4	Specific gravity of solution.
A4 BC D4 E4 GH L4 L4	Na ₂ SO ₄ K _S SO ₄ KCl. NaCl. NaSO ₄ and aphthitalite. K _S SO ₄ and aphthitalite. KCl and K ₂ SO ₄ . KCl and NaCl. NaCl and Na ₂ SO ₄ . K _S SO ₄ . KCl aphthitalite.	37.75 27.87 35.46	49.70	42.06 10.09	11.77 18.60 2.12	1, 286 1, 120 1, 204 1, 183 1, 332 1, 183 1, 249 1, 210 1, 223
M4 N4	KCl, NaCl, áphthitalite NaCl, Na ₂ SO ₄ , aphthitalite	25. 45 28. 28	29.38 15.72	3, 33 8, 88		1. 257 1. 253

Table 6.—Composition of solutions saturated with certain salts at 75° C.—Con.

In mols per 1,000 mols of water.

	Saturated with—	Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K2SO4	Sum.
A4	Na ₂ SO ₄			55. 03	21.50	55. 21.
	KClNaCl.	58. 17	60.02			60. 58.
£4 £4	Na ₂ SO ₄ and aphthitalite K ₂ SO ₄ and aphthitalite			53. 34 12. 80	12.17 19.23	65. 32.
14 14	KCl and K ₂ SO ₄ KCl and NaCl NaCl and Na ₂ SO ₄	42.94	58. 90 35, 11	8.48	2, 19	61 78 63
4	K ₂ SO ₄ , KCl, aphthitalite KCl. NaCl, aphthitalite	8. 80 39. 23	51. 45 35. 50	4. 23	2, 93	63 78
Ĭ.	NaCl, Na ₂ SO ₄ , aphthitalite	43. 57	18.99	11.26		73

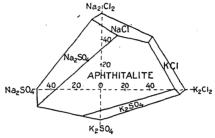


FIGURE 10.—Equilibrium diagram of certain salts at 100° C. Figures indicate mols per 1,000 mols of water.

Table 7.—Composition of solutions saturated with certain salts at 100° C.

In grams per 100 grams of water.

Saturated with—	NaCl	KCl	Na ₂ SO ₄	K2SO4	Specific gravity of solution.
Na ₂ SO ₄			41.68	23.44	1. 264 1. 134
NaCl	30.40				1 217 1 175
Naso4 and aphthitalite K ₂ SO ₄ and KCl		54 43	13. 57	20. 51	1.326 1.213 1.225
NaCl and KCl NaCl and Na ₂ SO ₄ .	27.39 36.56	35.16	6.41		1. 253 1 204
KCl, NaCl, aphthitalite	24.82	50.01 36.13	43.77		1. 233 1. 269 1. 256
	Na ₂ SO ₄ K ₂ SO ₄ K ₂ SO ₄ NaCl. Na ₂ SO ₄ and aphthitalite K ₂ SO ₄ and aphthitalite K ₂ SO ₄ and KCl NaCl and KCl NaCl and Na ₂ SO ₄ . K ₂ SO ₄ , KCl, aphthitalite. K ₂ SO ₄ , KCl, aphthitalite.	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Na ₂ SO ₄ . K ₂ SO ₄ . K ₂ SO ₄ . K ₂ SO ₄ . Na ₂ SO ₄ and aphthitalite. K ₂ SO ₄ and aphthitalite. K ₂ SO ₄ and kCl. Na ₂ SO ₄ and kCl. S ₂ SO ₄ and kCl. Na ₂ SO ₄ and kCl. S ₃ SO ₄ and kCl. S ₄ SO ₄ and kCl. NaCl and KCl. NaCl and Na ₂ SO ₄ . S ₅ SO ₄ KCl, aphthitalite. S ₅ SO ₄ KCl, aphthitalite.	Na ₂ SO ₄ . 41.68 K ₂ SO ₄ 56.20 NaCl 39.40 41.70 Na ₂ SO ₄ and aphthitalite 39.40 41.70 K ₂ SO ₄ and aphthitalite 54.43 Na ₂ SO ₄ and KCl 54.43 NaCl and KCl 27.39 35.16 NaCl and Na ₂ SO ₄ 38.56 6.41 K ₂ SO ₄ KCl, aphthitalite 31.9 50.01 K ₂ SO ₄ KCl, aphthitalite 31.9 50.01 K ₂ SO ₄ KCl, aphthitalite 24.82 36.13 43.77	Na ₂ SO ₄ . 41.68 K ₃ SO ₄ . 23.44 K ₃ SO ₄ . 56.20 Na ₂ SO ₄ and aphthitalite. 39.40 Na ₂ SO ₄ and aphthitalite. 13.57 K ₃ SO ₄ and aphthitalite. 13.57 Na ₂ SO ₄ and KCl. 13.62 K ₃ SO ₄ and KCl. 27.39 NaCl and KCl. 27.39 NaCl and Na ₂ SO ₄ 35.16 NaCl and Na ₂ SO ₄ 36.56 Na ₂ SO ₄ KCl, aphthitalite 31.9 Na ₂ SO ₄ 36.13 Na ₂ SO ₄ 36.

In mols per 1,000 mols of water.

	Saturated with—	Na ₂ Cl ₂	K ₂ Cl ₂	Na ₂ SO ₄	K ₂ SO ₄	Sum.
A ₅ B ₅ C ₅	Na ₂ SO ₄			52.86	24. 07	52.86 24.07 67.90
D ₅ E ₅ F ₅	KCl. NaCl. Na ₂ SO ₄ and aphthitalite K ₂ SO ₄ and aphthitalite	60.81				60. 81 66. 96 38. 42
Gs Hs	R ₂ SO ₄ and KCl. NaCl and KCl. NaCl and Na ₂ SO ₄ .	42, 20	65. 76 42. 48	8. 12	2. 93	68, 69 84, 68 64, 45
Is Ls Ms Na	K ₂ SO ₄ , KCl, aphthitalite. KCl, NaCl, aphthitalite. NaCl, Na ₂ SO ₄ , aphthitalite.	4. 91 38. 25	60. 41 43. 65 12. 31	4.78	3. 24 11. 37	68. 56 86. 68 78. 90

SALT CAKE.

Salt cake is obtained in large quantities in the manufacture of hydrochloric acid from common salt, by the action of either niter cake or sulphuric acid. The process is usually carried out by placing about half a ton of salt in a large semispherical pan set in brickwork and heated by direct firing. An equal weight of concentrated sulphuric acid is added from a leaden cistern, when the following chemical reaction takes place:

The hydrochloric acid that escapes through a flue in the dome of brickwork that covers the pan is absorbed by water. The hot mass is then raked into a muffle furnace, where the reaction is completed at a higher temperature:

The additional hydrochloric acid escapes through a separate flue and, after being cooled and washed, is also absorbed by water in special absorbing devices made of acid-proof materials.

Hydrochloric acid is used as a laboratory reagent and for many minor industrial purposes. The production of this acid in the United States in 1919, as reported by the Bureau of the Census, amounted to 150,000 tons, valued at \$4,312,000. It can readily be seen that an increased demand for salt cake might lead to lower prices for hydrochloric acid. But hydrochloric acid is also made by a catalytic process from chlorine, which is a by-product of the electrolytic caustic-soda industry, and hydrogen, which is a by-product of the electrolytic oxygen industry. It appears, therefore, that changes caused by an increased demand for salt cake may affect several other industries to a certain extent.

Salt cake is made in England by Hargreave's process, which uses salt, sulphur dioxide, air, and steam.

Attempts have been made from time to time to vary the apparatus used in making salt cake—for example, to use mechanical or continuous furnaces—but without effecting important changes.

From 1910 to 1915 the prices recorded for salt cake in the trade journals showed little variation, ranging from about \$10 to \$13 a ton for ground material. In 1916 the quotation fell to \$8, but immediately afterward it began a rapid rise which continued through 1917 and nearly all of 1918 and carried prices up to \$40. Early in 1919, however, they had fallen back to \$13 and even went as low as \$10. In the early part of 1920, on account of the insistent demand for export, they began rising again until \$60 was bid for small quantities in the spot market, when such supplies were practically

exhausted. Long-term contracts, however, were made at \$30 to \$35 a ton at this time, and in the closing months of the year salt cake was offered rather freely at \$30 a ton. The Engineering and Mining Journal in December, 1920, quoted sodium sulphate at mines in Idaho and Arizona at \$18 to \$22 a ton.

The range of prices up to the latest date available is shown in Figure 11.

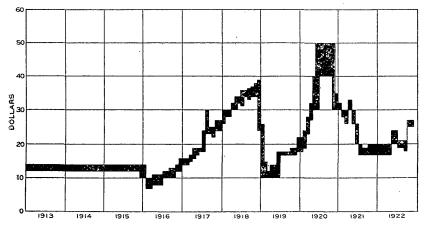


FIGURE 11.-Prices per ton of salt cake in the New York chemical market, 1913-1922.

The salt cake marketed in the United States, as reported to the United States Geological Survey for certain years and to the Bureau of the Census for 1914 and 1921, was as follows:

TABLE 8.—Salt cake marketed in the United States in 1914 and 1917-1921.

c :	Tons.	Value.
1914	90, 440 183, 910	· \$841,900
1918.	141, 050	2, 844, 900
1919.	129, 000	2, 019, 400
1920.	178, 770	2,049,100
1921	91, 900	1,955,500

The following firms produced sodium sulphate as salt cake in 1920:

Butterworth-Judson Corporation, 61 Broadway, New York, N. Y.

Consolidated Chemical Co., Lompoc, Calif.

Contact Process Co., P. O. Drawer 98, Buffalo, N. Y.

E. I. du Pont de Nemours & Co., Wilmington, Del. ,

General Chemical Co., New York, N. Y.

Grasselli Chemical Co., Cleveland, Ohio.

Kalbfleisch Corporation, 31 Union Square west, New York, N. Y.

Charles Lennig & Co., Philadelphia, Pa.

Merrimac Chemical Co., 148 State Street, Boston, Mass.

Monsanto Chemical Works, St. Louis, Mo.

Mutual Chemical Co. of America, 99 John Street, New York, N. Y. Naugatuck Chemical Co., Elm Street, Naugatuck, Conn.

New Jersey Zinc Co., 160 Front Street, New York, N. Y.

Pennsylvania Salt Manufacturing Co., Philadelphia, Pa.

Powers-Weightman-Rosengarten Co., Philadelphia, Pa.

rowers-weightman-kosengarten Co., Finiadelphia, Fa.

Rollin Chemical Corporation, Equitable Building, New York, N. Y.

In addition to salt cake the Census Bureau reported the production of 2,020 tons of refined anhydrous sodium sulphate, valued at \$154,000, in 1921, as compared with 2,708 tons, valued at \$221,232, in 1919.

GLAUBER'S SALT.

The necessary conditions for the preparation of Glauber's salt are evident from the solubility diagram, Figure 5. The yield is enormously increased by chilling; the salt can not be obtained at all above 32.4° C. This salt is used in dyeing and medicine. On account of its high content of water, however, it is an expensive form in which to transport sodium sulphate in bulk. As much of the natural sodium sulphate occurs in this form the principal chemical engineering problem in placing it on the market is the profitable dehydration of the hydrated compound.

The Glauber's salt marketed in the United States in recent years is shown below. The figures for 1909, 1914, and 1921 are those of the Census Bureau.

Table 9.—Glauber's salt produced in the United States in 1909, 1914, and 1917-1921.

	Tons.	Value.
1909 1914 1917 1918 1919 1920	34, 540 46, 470 47, 760 50, 720 47, 730 50, 660 52, 040	\$427,800 512,500 732,400 1,041,100 877,060 990,540 1,289,000

The following firms produced Glauber's salt in 1920:

Atlantic Carbonic Co., 268 Third Street, Chelsea, Mass.

Chicago Copper & Chemical Co., 111 West Jackson Boulevard, Chicago, Ill.

Columbus Crystal Co., 15 Arch Street, Newark, N. J.

Consolidated Chemical Co., Lompoc, Calif.

E. I. du Pont de Nemours & Co., Wilmington, Del.

General Chemical Co., New York, N. Y.

Gill Soda Co., Cheyenne, Wyo.

Grasselli Chemical Co., Cleveland, Ohio.

Iowa Soda Products Co., Council Bluffs, Iowa.

Kalbfleisch Corporation, 31 Union Square west, New York, N. Y.

Charles Lennig & Co. (Inc.), Philadelphia, Pa.

Merrimac Chemical Co., 148 State Street, Boston, Mass.

Powers-Weightman-Rosengarten Co., Philadelphia, Pa.

Stauffer Chemical Co., 624 California Street, San Francisco, Calif.

NITER CAKE.

Niter cake, the residual product in the preparation of nitric acid from sodium nitrate (Chile saltpeter) and concentrated sulphuric acid, varies somewhat in composition according to the temperature used in the reaction. If the heating is not carried to a high point some NaHSO₄ is present; otherwise only Na₂SO₄ and Na₂S₂O₇. Manufacturers report either the percentage of acid sulphate, NaHSO₄, or the percentage of sulphuric acid in the product; the latter generally ranges from 25 to 35 per cent.

A list of uses that have been suggested for niter cake would be too long to give here. The reader who is interested is referred to an article by J. Johnston in the Journal of Industrial and Engineering Chemistry for June, 1918, and a committee report in the Journal of the Society of Chemical Industry, volume 34, page 1121, 1915. Many makers of niter cake consume their entire product in their own works. The niter cake marketed in the United States, as reported to the United States Geological Survey for certain years and to the Census Bureau for 1914 and 1921, was as follows:

Table 10.—Niter cake sold in the United States in 1914 and 1917-1921.

	Tons.	Value.
1914. 1917. 1918. 1919. 1920.	387, 800 143, 200 83, 400 308, 640	\$31,600 780,200 595,700 271,400 788,540 255,100

The following firms reported sales of niter cake in 1920:

Aetna Explosive Co., New York, N. Y.

American Steel & Wire Co. of New Jersey, 503 Western Reserve Building, Cleveland, Ohio.

American Zinc & Chemical Co., Oliver Building, Pittsburgh, Pa.

Atlas Powder Co., 140 North Broad Street, Philadelphia, Pa.

Butterworth-Judson Corporation, 61 Broadway, New York, N. Y.

Charles Cooper & Co. (Inc.), 194 North Street, New York, N. Y.

Davison Chemical Co., Baltimore, Md.

E. I. du Pont de Nemours & Co., Wilmington, Del.

Eagle-Pitcher Lead Co., Box 770, Chicago, Ill.

General Chemical Co., New York, N. Y.

Grasselli Chemical Co., Cleveland, Ohio.

Kalbfleisch Corporation, 31 Union Square west, New York, N. Y.

Charles Lennig & Co. (Inc.), 112 South Front Street, Philadelphia, Pa.

Merrimac Chemical Co., 148 State Street, Boston, Mass.

Monsanto Chemical Works, St. Louis, Mo.

Naugatuck Chemical Co., Naugatuck, Conn.

Powers-Weightman-Rosengarten Co., Philadelphia, Pa.

Tennessee Copper Co., 61 Broadway, New York, N. Y.

Victor Chemical Works, Fisher Building, Chicago, Ill.

NATURAL SODIUM SULPHATE.

Sodium sulphate is found as a constituent of surface salts or lake waters in many of the dry districts of Arizona, California, New Mexico, Nevada, Oregon, Utah, Washington, and certain foreign countries. When this salt crystallizes from water in which sodium chloride is not present in large quantity, the mineral formed is mirabilite; with higher concentrations of salt or at higher temperatures, however, then ardite is the stable form, as is evident from Figures 1–4.

ORIGIN.

The origin of sodium sulphate in certain deposits and saline lakes is easily explained. In tunnels, caves, and covered spots in recent lavas, such as those on the Island of Hawaii, white coatings, powders, and efflorescences consisting largely of calcium and sodium sulphates are frequently observed. Rain water dissolves these coatings where it has access to them. This shows that basalts and lavas may furnish sodium sulphate to drainage systems. Moreover, granite and other igneous rocks are rarely free from pyrite and other sulphides. The sulphides on exposure are oxidized to sulphuric acid, which immediately dissolves some of the basic oxides, producing soluble sulphates.

Hardly any natural water can be found that is entirely free from sulphates. In most regions, however, such waters eventually escape to the ocean. In arid districts and the great closed basins, where rainfall is deficient and there is no outlet to the ocean, the soluble salts accumulate and may eventually form a deposit that is fairly dry for part of each year.

As an intermediate stage, even in waters that contain a relatively small proportion of sodium sulphate, mirabilite may be deposited in cold weather. The conditions that accompany this deposition generally involve the presence of some wind-blown sand, which may cover the precipitated sodium sulphate, or silt may effect the same result. In consequence of being more or less covered and on account of the high density of the saturated solution the salt is dissolved more slowly than it was precipitated and perhaps is not entirely redissolved in an entire season. Thus an accumulation is brought about. Subsequently the water area shifts or the lake dries up, leaving the salt or salts deposited in the form of a hard layer or salt-incrusted sand.

Some other possible methods of origin might be mentioned. For instance, the concentration and evaporation of many river waters, especially those of the Western States, which contain principally calcium bicarbonate, would cause a deposition of calcium carbonate and

leave a solution rich in sodium sulphate, with smaller amounts of magnesium sulphate and sodium chloride.

Owing to the fact that soils consist largely of decomposed rock, sodium sulphate is a natural minor constituent of soils but one which is of course almost entirely removed by leaching where rainfall and drainage are normal. In the more arid regions, however, it accumulates and is called white alkali, as previously mentioned. Glauber's salt is a common constituent of efflorescences on clays in dry regions.

DEPOSITS.

The following notes on occurrences of natural sodium sulphate, which have been compiled with the assistance of Miss M. R. Nourse and other members of the United States Geological Survey, represent information that has come from many scattered sources. Although many of these occurrences are well known and some are now being worked, others have not been investigated by the United States Geological Survey and probably can not be considered of commercial value. At some of the localities only single samples have been taken, and of course further investigation of the extent and quality of such deposits would be required before any estimate of their value could be given. A few foreign occurrences are also listed for comparison.

ARIZONA.

Santa Catalina, Pima County.—Loew ⁵ gave an analysis of an efflorescence consisting of 94 per cent Na₂SO₄ found at Santa Catalina, Pima County, Ariz., but mentioned no details of the extent of the deposit.

Verde Valley.—The occurrence of thenardite in Verde Valley is described by Blake.⁶ The salt is found about 4 miles north of Squaw Peak, half a mile west of the river, in ledges or benches and rounded hills about 50 feet above the river. It is evidently a deposit from an ancient lake. The deposit covers many acres and is possibly 50 feet thick, and the available tonnage therefore runs into the millions. Mirabilite, blue halite, and glauberite were also noted by Blake near the deposit. The nearest point on the railroad is Clarkdale, about 20 miles distant.

The deposit is now being worked by the Western Chemicals Corporation, 401 Broadway, New York City, which states that several shafts sunk in the deposit have shown very clean anhydrous material. The corporation contemplates the installation of refining

⁵ U. S. Geol. Surveys W. 100th Mer. Rept., vol. 3, p. 628, 1875.

⁶ Blake, W. P., Am. Jour. Sci., 3d ser., vol. 39, p. 43, 1890.

equipment, however, so that material of lower grade can be recrystallized and a pure salt cake produced.

CALIFORNIA.

Carrizo Plain.—The deposit in Carrizo Plain, San Luis Obispo County, Calif., known as Soda Lake has been described by Arnold and Johnson ⁷ and by Gale. ⁸ Gale estimated the probable quantity of sodium sulphate available for commercial utilization here at over a million tons. The salt occurs in a relatively thin crust, a few inches thick, with possibly some "channels" of greater thickness. Transportation to the nearest railway station, McKittrick, involves a haul of 16 miles over a grade. This deposit has been worked for many years by the Consolidated Chemical Co., of Lompoc, Calif. Part of the product is said to be used by the Torrance Window Glass Co., Torrance, Calif.

Imperial Valley.—A recent application to the General Land Office to prospect for potash contained mention of the occurrence of a ledge of sodium sulphate in sec. 24, T. 9 S., R. 11 E., in the northern part of Imperial County, near the station of Bertram, on the Southern Pacific Railroad. This locality adjoins Salton Sea, formerly a dry lake or playa known as the Salton Sink.

Kern County.—Sodium sulphate occurs about half a mile northeast of Buckhorn Springs, 6 miles south of Munroe, Kern County, as shown by tests in the chemical laboratory of the United States Geological Survey on material collected by D. G. Thompson from holes in two circular depressions between 500 and 100 feet in diameter, the surface of which was rough, soft, and practically bare of vegetation. Water stood in the holes within a foot of the surface of the ground. The material effloresced shortly after collection, and when analyzed it was practically free from moisture. No examination has been made to determine the extent of the deposit.

Mohave Desert.—The possibility of utilizing the sodium sulphate occurring in the Mohave Desert involves its separation from sodium chloride. As this would have to be done by chilling, it does not appear to warrant consideration except as a possibility in cold weather, in view of the existence of other natural brines carrying almost pure sodium sulphate.

Mono Lake.—Although the water of Mono Lake contains sodium sulphate, the total concentration of salts is only about 5 per cent,

⁷ Arnold, Ralph, and Johnson, H. L., Sodium sulphate in Soda Lake, Carrizo Plain, San Luis Obispo County, Calif.: U. S. Geol. Survey Bull. 380, pp. 369-371, 1909.

⁸ Gale, H. S., Sodium sulphate in the Carrizo Plain, San Luis Obispo County, Calif.: U. S. Geol. Survey Bull. 540, pp. 428-433, 1914.

and the salts include sodium chloride and sodium carbonate. therefore evident that the sodium sulphate could be recovered only as a by-product in the preparation of sodium carbonate.

Owens Lake.—None of the companies working the water of Owens Lake for trona and soda ash have reported the production of sodium As shown by the analyses in Table 11, however, the proportion of sulphates in the water of Owens Lake is less than the proportion in Mono Lake or that in Searles Lake, and the salt, if recovered from the mother liquor after removal of the sodium bicarbonate, would have to be separated from a solution carrying much sodium chloride. For the reason already stated this separation does not appear to be commercially feasible.

Table 11.—Analysis of waters from saline lakes of high sulphate content.

	1	2	3	4	5	6	7	8
Cl	22.64	25. 01	20. 26	0.87	12.50	8. 68	10.13	35.89
SO ₄ CO ₃	12.47 19.78	9.74 19.56	20.77 19.55	61.55 1.00	15.47 22.77	58. 17	52.47 1.08	13.72 5.68
HCO ₃ B ₂ O ₄	5.92	4.29		7.99	11.55		6.10	1.63 2.18
B ₄ O ₇	.30	1.88 37.25	35.79	20,00		2.05 26.97	25. 03	32.78
K	1.80	2.05	2.44	1.22	37.27			7.10
CaMg.	.10		.28	1.05 6.06	Trace.	. 93 3. 20	5.19	
SiÔ2 Al ₂ Ô3	. 13	. 22	.65	. 21	. 40			
Fe ₂ O ₃	Trace.			. 05				
Salinity, parts per million	100.00 51.068	100.00 111,930	100.00 4,910	100.00 6,708	100.00 28,195	100.00 52,600	100.00 11,623	100.00 343,500

Searles Lake.—As shown by the analysis in Table 11 the brine at Searles Lake may be made to yield several different salts. early days borax was obtained; a more recent project attempted the precipitation of sodium bicarbonate; but the plants at present operating at the lake are concerned chiefly with the extraction of potassium chloride and borax. When the writer visited the plant of the American Trona Corporation, in September, 1920, it was stated that the process then being used in making potassium chloride and borax involved the early separation of most of the sodium sulphate and sodium carbonate. As these salts are presumably mixed with a con-

^{1.} Mono Lake, 1882. Analysis by T. M. Chatard, U. S. Geol. Survey Bull. 60, p. 53, 1890. Specific gravity 1.045.
2. Owens Lake, 1912. Analysis by W. B. Hicks in the laboratory of the U. S. Geol. Survey. Specific gravity 1.0977.
3. Tulare Lake, February, 1889. Analysis by E. W. Hilgard, California Univ. Coll. Agr. Appendix to Twelfth Rept., for 1890, p. 42, 1892. This lake has an outlet during floods but not at other times. An analysis of water collected in 1880 is also

during floods but not at other times. An analysis of water collected in 1880 is also given.

4. Lake De Smet, Wyo. Analysis by W. T. Schaller. An analysis of its feeder, Shelle Creek, was also made. See U. S. Geol. Survey Water-Supply Paper 364, p. 17, 1914.

5. Soap Lake, Wash. Analysis by George Steiger, U. S. Geol. Survey Bull. 113, p. 113, 1893.

6. Big Lake, Union Pacific Group, Wyo. Analysis by Pemberton and Tucker, Chem. News, vol. 68, p. 19, 1893. Specific gravity 1.0487.

7. Devils Lake, N. Dak. Analysis by H. W. Daudt, North Dakota Univ. Quart. Jour., vol. 1, p. 225, 1911. Reduced to standard form: Ca, 0.04; SiO₂, 12.2; R₂O₃, 4.0 parts per million.

8. Searles Lake, Calif. Analysis by R. C. Wells. Jour. Ind. Eng. Chemistry, vol. 13.

^{8.} Searles Lake, Calif. Analysis by R. C. Wells. Jour. Ind. Eng. Chemistry, vol. 13, p. 691, 1921.

siderable amount of sodium chloride, however, it appears doubtful whether their separation would be profitable under present conditions.

Tulare Lake.—The water of Tulare Lake is a dilute water, yielding on evaporation sodium sulphate, carbonate, and chloride.

COLORADO.

In 1870 it was reported that 3 tons a day of crude soda could be made from the soda springs about 10 miles southwest of Denver, in Jefferson County, Colo. The water of the small ponds between Bear Creek and Turkey Creek was reported to contain 20 per cent of sodium sulphate, carbonate, and chloride, and the surrounding earth 33 per cent of these salts.

In a later report similar statements were made concerning Burdsalls Soda Lakes, four in number, 12 miles south of Denver. The solid salt around the margins of the lakes was shown to be crude sodium sulphate. No recent information concerning these waters has come to the attention of the writer.

IDAHO.

Some deposits of sodium sulphate, called the Claytonia claims, in T. 2 N., R. 5 W., just west of Jump Creek, western Idaho, have been described by Mansfield, 12 from whose account it appears that similar deposits occur intermittently over a considerable area between Jump Creek and Sucker Creek, Oreg. (see p. 26), but their extent has not been sufficiently determined to place an estimate on their commercial value.

NEVADA.

Brown's Station.—An analysis of the incrustation found on the soil of the desert west of Humboldt Lake is given in the final report of the King Survey.¹³

Analysis of incrustation on soil at Brown's Station, west of Humboldt Lake, Nev.

[R. W. Woodward, analyst.]

Soluble	in water, 27.71 per cent.	
Sodium	chloride	49.67
Sodium	sulphate	20.88
Sodium	sesquicarbonate	18. 15
Sodium	borate	11.30
	•	
		100.00

⁹ Wilson, J. S., General Land Office Rept. for 1870, p. 120.

¹⁰ Smith, J. A., Colorado Geol. Survey Rept. for 1881-82, p. 117.

U. S. Geol. Survey Terr. Fourth Ann. Rept., p. 187, 1872.
 Mansfield, G. R., Nitrate deposits in southern Idaho and eastern Oregon: U. S. Geol.
 Survey Bull. 620, pp. 19-44, 1915.

¹⁸ Hague, Arnold, U. S. Geol. Expl. 40th Par. Rept., vol. 2, p. 744, 1877.

This analysis is not given to suggest commercial possibilities but rather to indicate the general character of the desert efflorescences. Under certain conditions similar deposits of considerable extent are formed from concentrated waters and become covered with silt or dust, which tends to preserve them. Such deposits are frequently located by drilling. The United States Geological Survey has done some drilling in the Black Rock and Smoke Creek deserts in Nevada in search of potassium compounds but has given little attention to the other salts. In material from many of the wells the percentage of soluble salts was small; in some of it sulphates and carbonates were found together with sodium chloride. The examination of these samples is still in progress.

Buena Vista Valley and other playa and spring deposits.—In the report cited above Hague 14 states that the alkali flat, about 12 miles in length by 4 miles in breadth, east of Buffalo Peak has around the edges and over much of the surface a heavy efflorescence of sodium chloride and sodium sulphate. The following analysis is given:

Analysis of efflorescence in Buena Vista Valley, Nev.

	[O. D. Allen, analyst.]	
NaCl		70.81
Na ₂ SO ₄		26.38
	·	
	-	99. 13

Buffalo Peak forms the south end of the Star Peak Range, which is the northern part of the Humboldt Range. The alkali flat lies about 11 miles east of the Rochester mining district, which has been described by Schrader. Material of the above-stated composition, if present in large quantity and so situated as to be capable of extraction, might conceivably be worked for sodium sulphate, but the present prices of sodium sulphate hardly warrant consideration of that possibility.

The alkali flat in Buena Vista Valley is merely one of the many in Nevada that were at one time parts of Lake Lahontan. The salt residues in such flats or playas may be regarded as residues left by evaporation of the former lake.

Similar statements apply to the residues of Lake Bonneville and those in certain other basins. The salts are largely products of the weathering and leaching of the rocks that form the basin and more immediately of the surface soils and sediments. On the other hand, a good many hot springs are to be found whose boron content suggests that they are of magmatic origin. Sulphates may have come from either source, magmatic or surface, although the oxidation of

Hague, Arnold, U. S. Geol. Expl. 40th Par. Rept., vol. 2, p. 731.
 Schrader, F. C., The Rochester mining district, Nev.: U. S. Geol. Survey Bull. 580, pp. 325-372, 1915.

sulphides at the surface has generally been considered the principal source of sulphates.

The products of the evaporation of spring waters form considerable deposits near several of the springs in Nevada-for example, at Sou Hot Springs, in the valley east of Buena Vista Valley, formerly called Osobb Valley; at Good Springs, Clark County; and at the springs east of Granite Mountain, on the western border of the Smoke Creek Desert. These occurrences, which all show more or less sodium sulphate, are interesting as showing a possible source of sodium sulphate in the sinks and plava lakes of the State. far as present information goes none of them are of commercial The samples taken may havé represented very small importance. deposits. More prospecting and chemical study is needed to show the relations of the several salts in these localities. Sodium sulphate has been noted as localized in the center of some playa lakes and around the edges of others. The exact reason for these differences is not clearly understood, but they are doubtless partly dependent on the variations of water level and temperature. Borings in Dixie Valley vielded brines in which sodium chloride is the principal constituent. 16

Even if sodium sulphate was deposited before sodium chloride in the evaporation of the former lakes and therefore in general should be sought above the lowest drainage levels, it must be remembered that more or less periodic leaching of such deposits would be certain to occur and destroy to some extent the natural sequence of deposition that might be expected from the solubilities of the salts.

Sodium sulphate is the chief mineral salt in the water of Schaffer's hot spring, near the north shore of Honey Lake, and in the water of the springs a few miles north of Granite Mountain. According to Russell, 17 Schaffer's spring was flowing copiously during the existence of Lake Lahontan. No analysis of the water of Honey Lake is available, but it is known to carry chiefly sodium chloride, sulphate, and carbonate. In the water of Walker Lake, which is, however, not very concentrated, the proportions of sodium sulphate and sodium carbonate in the total salts are relatively high.

Mina.—Sodium sulphate was mentioned in unpublished notes by H. S. Gale as occurring "near Mina, Nev.," in a deposit along a zone of faulting and hydrothermal action, but no further details are available.

Ragtown Soda Lakes.—The soda lakes near Ragtown have been described by King, 18 Hague, 19 Russell, 20 and Chatard, 21

¹⁶ Young, G. J., Potash salts and other salines in the Great Basin region: U. S. Dept. Agr. Bull. 61, p. 54, 1914.

17 Russell, I. C., Geological history of Lake Lahontan: U. S. Geol. Survey Mon. 11,

King, Clarence, U. S. Geol. Expl. 40th Par. Rept., vol. 1, pp. 510-513, 1878.
 Hague, Arnold, idem, vol. 2, pp. 746-750, 1877.
 Russell, I. C., op. cit., pp. 73-80.
 Chatard, T. M., U. S. Geol. Survey Bull. 60, pp. 46-53, 1890.

they have been worked chiefly for sodium carbonate, the analysis by F. W. Taylor, which is cited by Russell, of material that was marketed in the early days shows about as much sodium sulphate as sodium carbonate. This material was probably "winter soda," naturally high in sulphate. Chatard showed that later operators were able to make "summer soda," which was essentially the mineral trona. The quantity of sodium sulphate in the water of the larger lake was estimated by Russell at about 340,000 tons, which is small when compared with many known deposits of natural sodium sulphate.

Silver Peak.—Glauber's salt has been reported as occurring in the southwestern part of the Big Smoky Valley, about 12 miles north of Silver Peak. The material as it occurs in the ground has a dark color and carries only about 50 per cent of Glauber's salt, which would have to be extracted and recrystallized. Water can not be obtained at the deposit. The quantity of Glauber's salt available is not known.

Smoke Creek Desert.—An early analysis of the surface incrustation of Smoke Creek Desert ²² is as follows:

Analysis of salts at Hardin City, Nev.

	[O. D. Allen, analyst.]	
Sodium	chloride	18.47
Sodium	carbonate	52. 10
Sodium	sulphate	27.55
		98, 12

Borings made by the United States Geological Survey show the presence of gaylussite in the mud of the playa, but as the salts were examined principally with reference to their potassium content much more detailed investigation will be needed to block out the relation of the other compounds.

Wabuska.—Russell ²³ mentions a deposit 6 to 8 feet thick of clear transparent crystals of sodium sulphate, resting on saline clay, formed by the evaporation of the waters of hot springs in Mason Valley, Lyon County, about 1 mile north of Wabuska station. The springs occur in a line that coincides with the course of a post-Lahontan fault.

NEW MEXICO.

Dona Ana County.—A deposit of sodium sulphate lies about 25 miles west of Valmont, N. Mex., between the San Andres Mountains and the white gypsum sands that are a prominent feature in the central part of the valley about 17 miles west of the railway. The roads between the deposit and the railway are reported to be fairly level, thus permitting hauling by autotruck.

²² Hague, Arnold, U. S. Geol. Expl. 40th Par. Rept., vol. 2, p. 792, 1877.

²³ Russell, I. C., op. cit., p. 48.

According to the description by Meinzer ²⁴ the alkali flat, the white sands, and much of the rest of the valley in this part of the Tularosa Basin is underlain by gypsum, the horizontal bedding of which near the alkali flat indicates deposition from a former lake. The flat is believed to have been excavated by wind action. Sodium sulphate is a prominent constituent of the solid material lying in

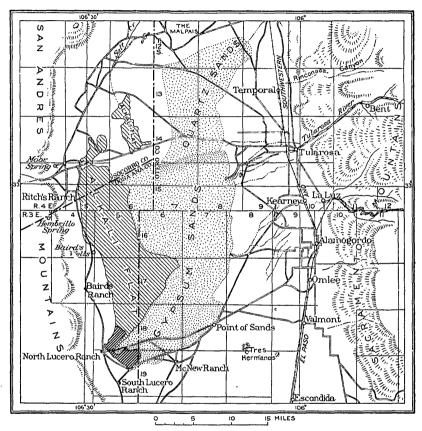


FIGURE 12.-Map showing alkali flat in Dona Ana County, N. Mex.

the lowest part of the flat, about in the south-central part of T. 18 S., R. 5 E. (See Fig. 12.)

In a sample of the solid material submitted by a person having an interest in the property above described, which was said to be representative of the whole deposit to a depth of 1 to 4 feet, the writer made a careful search for the mineral glauberite but could not detect any. The sample appeared to consist entirely of gypsum more or less coated and mixed with sodium sulphate, most of which was apparently anhydrous. It is presumed that the sample was col-

²⁴ Meinzer, O. E., Geology and water resources of Tularosa Basin, N. Mex.: U. S. Geol. Survey Water-Supply Paper 343, p. 69, 1915.

lected during a dry period or had been allowed to dry out in the air, for it is understood that water will generally rise nearly to the surface in any pits that are dug in the lowest parts of the flat. This feature is important in considering the commercial value of the deposit, for the water standing in the pits and filling the pores in the solid material is naturally very nearly saturated with sodium sulphate at the temperatures prevailing in this region. Such a solution could either be evaporated to yield all of its dissolved sodium sulphate, which would include any other soluble salts present in the water, or chilled to yield Glauber's salt, which could be sold as such or converted into the anhydrous salt.

The Southern Chemical Co., of El Paso, Tex., did some experimental work on the production of anhydrous sodium sulphate from this deposit in 1919. It was later reported to have been taken under the control of the Great Southern Sulphur Co., a New Orleans concern. An application for commodity freight rates on the product was granted in April, 1919. The present rates are about \$7.20 a ton to Kansas and Oklahoma points, \$9.90 to Colorado, Missouri River points, and Galveston, \$12 to Chicago, and \$19 to Baltimore and New York.

It is obvious that as regards its utility this source of sodium sulphate is one step removed, so to speak, from deposits of Glauber's salt itself, but it has the advantage of being less contaminated with other salts than many saline waters which carry sodium sulphate as their chief constituent.

Laguna Salina.—The occurrence of salt at Laguna Salina, in T. 5 N., R. 10 E., Torrance County, has long been known, the salt having been used for cattle in very early times. The lake, which is usually dry, covers about 670 acres. Crystals of bloedite have been reported as occurring in the black mud about 2 feet beneath the surface of the lake. Mirabilite has also been reported. The deposit is apparently of no value, however, for sodium sulphate.

OREGON.

Harney Lake.—An analysis given by Clarke ²⁵ shows that the water of Harney Lake, Oreg., resembles that of Owens Lake, Calif., but is much less concentrated and contains relatively less carbonate and sulphate and consequently more chloride.

Sucker Creek.—In secs. 11 and 12, T. 23 S., R. 46 E. Willamette meridian, east of Sucker Creek, some low hills have been found to carry Glauber's salt in beds 2 feet or more thick. The salt is partly effloresced in the upper 3 or 4 inches. A claim of 120 acres, called

²⁵ Clarke, F. W., The data of geochemistry, 4th ed.: U. S. Geol. Survey Bull. 695, p. 159, 1920.

the American placer, has been located in these deposits by the American Fertilizer Co. These deposits are described briefly by Mansfield.²⁶

TEXAS.

A lake about 11 miles from the railroad at Monahans, Ward County, Tex., is reported to be underlain by at least one and possibly two thin beds of crystallized salts, which appear to be chiefly Glauber's salt, according to the results of an inspection of a single sample made in the chemical laboratory of the United States Geological Survey. The lake is reported to have an area of about 160 acres. The first layer of salts, from 3 to 6 feet thick, occurs at a depth of 1 to 3 feet below the surface of the lake. A second bed of salts has been noted about 30 feet lower, under intervening red clay. The sample mentioned was collected by J. D. Jones, of Monahans, from the lake, which is partly on his ranch. He states that a good road runs from Monahans to a point within a mile of the lake.

UTAH.

Great Salt Lake.—It was stated in 1920 27 that the Minerals Salt Co. had been incorporated to work deposits of Glauber's salt on the south shore of the Great Salt Lake, from which the Midwest Dye & Chemical Co. had already produced some salt cake. These deposits were said to be 5 to 7 feet thick and to be about half sand and also covered with about 2 feet of sand. The method of working consisted in removing the overburden of sand and injecting live steam into the pits until enough solution was accumulated to be pumped into a small settling tank. This solution was then decanted into shallow ponds, where pure Glauber's salt separated as the solution cooled. It was later reported that both of these companies had discontinued active operation, but that other persons were studying methods of working the deposits. The Utah Sodium Products Co., 1022 Kearns Building, Salt Lake City, has acquired an option on 700 acres on the lake front to cover part of the same deposit of sodium sulphate.

Sevier Lake.—Gilbert 28 mentions the occurrence of a crust of sodium suhphate about 2 inches thick in the center of Sevier Lake.

Wendover.—A specimen of material obtained near Wendover, on the western edge of the Salt Lake Desert, sent in for examination to the United States Geological Survey was found to carry 97.3 per cent of anhydrous sodium sulphate. The material was said to cover several acres.

²⁶ Mansfield, G. R., Nitrate deposits in southern Idaho and eastern Oregon: U. S. Geol. Survey Bull. 620, p. 30, 1915.

27 Chem. and Met. Eng., Dec. 29, 1920.

²⁸ Gilbert, G. K., Lake Bonneville: U. S. Geol. Survey Mon. 1, p. 225, 1890.

WASHINGTON.

Okanogan County.—Analyses of samples collected from small lakes east of Okanogan River at Malott, Okanogan County, Wash., have shown the material to be almost pure sodium sulphate. Details concerning the extent of the deposits are not available. Many small ponds in the hilly region along Okanogan River become almost or completely dry in the dry season and consequently yield saline deposits.

Some lakes in Kruger Mountain, west of Oroville, near the Canadian line, have yielded considerable quantities of magnesium sulphate in the form of the mineral epsomite (MgSO₄.7H₂O). This compound seems to be a more prominent constituent in the Canadian saline lakes than in those of the arid regions in the United States. Its value when unrefined is about the same as that of sodium sulphate.

The water of Omak Lake is essentially a rather dilute solution of sodium carbonate and sodium sulphate. It has been estimated that there is about 1,300,000 tons of these salts in the lake.

Grant County.—An analysis of a sample of water of Soap Lake, in Grant County, is given in Table 11. When this sample was collected the water was about as concentrated as sea water. The lake is therefore too dilute for direct commercial utilization, and the same may be said of a number of other so-called alkali lakes of this region.

WYOMING.

Carbon County.—The Bothwell saline deposits are in secs. 23 and 26, T. 25 N., R. 89 W., Carbon County, Wyo. The main deposit is about 750 by 1,500 feet in extent and over 2 feet thick, according to Knight,²⁹ who examined the deposits in 1899. The upper portion consists largely of Glauber's salt, with about 2 per cent of magnesium sulphate and from 1.8 to 4.2 per cent of silt. The lower portions contain more anhydrous sodium sulphate. The soils of the region are also rich in "alkali." Knight states that this material has clearly been derived from the decomposition of the Tertiary and Laramie formations, as they are the only ones that could supply them.

Sodium sulphate has also been reported to occur in the extreme southwestern township of Carbon County.

Downey Lakes, Albany County.—The Downey Lakes are about 22 miles southwest of Laramie and have been filled with soluble salts derived from Triassic sandstone and Jurassic clay, according to Knight. The beds in the lakes thicken toward the center and consist of Glauber's salt and magnesium sulphate. Bloedite has not

²⁰ Knight, W. C., and Slosson, E. E., Alkali lakes and deposits: Wyoming Univ. Exper. Sta. Bull. 49, 1901.

DEPOSITS. 29

been reported. Although the quantity of sodium sulphate in these lakes is very large, the deposit is far from the railroad, and to utilize the salts it would be necessary to separate the two sulphates. Other deposits in the State appear more promising.

Gill Lakes, Natrona County.—The deposits at the Gill Lakes, in Natrona County, worked commercially by the Gill Soda Co., are in sec. 26, T. 35 N., R. 78 W., about 12 miles northeast of Casper and about 7 miles from Fry station on the Chicago, Burlington & Quincy Railroad. The lakes are dry most of the year, but the deposits consist of Glauber's salt. The principal deposit, which is about 13 acres in extent, has been opened up to a depth of 22 feet in the solid salt, and preparations are now being made to refine the material so as to make it suitable for all the uses to which sodium sulphate is put.

Park County.—Holmes Lake, a small lake about 5 acres in extent, about $2\frac{1}{2}$ miles northwest of Cody, Park County, is reported to carry Glauber's salt. The United States Geological Survey has not examined it. An application to lease under the sodium mining law has also been made for a small lake southwest of Cody, in the N. $\frac{1}{2}$ SE. $\frac{1}{4}$ sec. 14, T. 52 N., R. 102 W.

Independence deposits, Natrona County.—Deposits that lie in old channels of Sweetwater River, somewhat north of its present course near Independence Rock, in the southwest corner of Natrona County, appear to be entirely superficial, lying in basins of mud that are largely impregnated with the salts. The deposits consist of thin crusts, in places 1 or 2 feet thick, of salts that are chiefly remarkable for their high proportion of sodium carbonate in spots. One of Slosson's analyses suggests that a layer of trona occurs in the Omaha claim, the salts of which are, however, only 3 or 4 acres in extent and about 4 feet deep in the middle. The Berthaton claims are the most northerly; the southern group consists of the New York, Philadelphia, Wilmington, Wilkesbarre, and Omaha claims. New York and Philadelphia claims cover 110 acres, the surface salts of which to the depth of a foot are largely sodium sulphate, according to Slosson. The origin of these salts is not settled, as the springs about the deposits yield very good water. It may be that the salts have been transported by the wind and retained by moisture in the lowest basins.

Lake de Smet.—The analysis of the water of Lake de Smet (T. 52 N., R. 82 W.) given in Table 11 shows that sodium sulphate is the principal constituent and magnesium sulphate next in importance, a very general relation in many Wyoming alkali lakes. The lake water had only 6,708 parts per million of total solids, however, in 1909. The water feeding the lake is much more dilute and carries

calcium carbonate as an abundant constituent, which seems to indicate that calcium carbonate must be precipitated as the lake evaporates.

Fremont County.—Analyses of a deposit near Pacific Springs and of another at an alkaline pond near Big Sandy Creek, in Fremont County, have shown 64 per cent or more of sodium sulphate.³⁰

Percy, Carbon County.—An analysis cited in the final report of the King Survey ⁸¹ shows that the saline matter in the clay of a small pond south of Percy consisted largely of sodium sulphate and magnesium sulphate.

Analysis of soluble matter in clay from shore of pond, Percy, Wyo.

[R. W. Woodward, analyst.]	
CaSO.	4, 45
MgSO ₄	
Na ₂ SO ₄	46, 27
NaCl	
•	99.74

Split Rock, Natrona County.—The small mud lake about 6 miles from Split Rock post office in secs. 19 and 20, T. 29 N., R. 88 W., Natrona County, is described by D. H. Attfield.³² The thin effloresced crust of sodium sulphate covers about 100 acres, but there is only 6 acres of deep salts, which consist of impure Glauber's salt with about 25 per cent of sand and mud.

Sodium, Natrona County.—Deposits of sodium sulphate are now being worked by the Gill Soda Co. about half a mile from the Chicago, Burlington & Quincy Railroad and the Chicago & Northwestern Railway at Sodium, Wyo. The quantity available is estimated at more than 250,000 tons.

Thermopolis, Hot Springs County.—Glauber's salt was identified as the principal mineral in a sample of material sent to the United States Geological Survey from Thermopolis.

Union Pacific Lakes, Albany County.—The Union Pacific Lakes, 13 miles southwest of Laramie, were visited by the writer in July, 1920. At that time they contained considerable water, but crystals of Glauber's salt were noted in water along the road that passes near the lakes, and it was reported that solid Glauber's salt exists in the mud under the lakes. Water is more abundant in the lakes since the Pioneer irrigating canal was built than formerly. A branch line from the Union Pacific Railroad to the lakes was removed some years ago. In 1885 the water of one lake was pumped into another so that the crude Glauber's salt could be harvested.

²⁰ U. S. Geol. Survey Terr. Fourth Ann. Rept., p. 188, 1872.

¹² U. S. Geol. Survey Expl. 40th Par. Rept., vol. 2, p. 148, 1877. ¹² Soc. Chem. Ind. Jour., vol. 14, p. 3, 1895.

It was allowed to effloresce somewhat in heaps and then shipped to the Laramie Chemical Works for conversion into salt cake, soda ash, and caustic soda. Two years later glassmaking was carried on for a time and some salt cake was shipped. The salt cake made in furnaces in Laramie in 1891 contained 96.37 per cent of sodium sulphate, 1.58 per cent of sodium chloride, and 2.05 per cent of magnesium sulphate. Since 1892 the deposits have not been worked. According to Slosson the apparatus used in dehydrating the Glauber's salt was not efficient.

CANADA.

Several lakes in western Saskatchewan have been reported to carry sodium sulphate in the form of mirabilite. At a lake near Oban the best crystals, left in the dry season, form a crust a few inches thick, but the greater part of the salt lies deeper, more or less mixed with mud. The water carries considerable magnesium sulphate and sodium chloride in addition to sodium sulphate. In some places the best crystals also contain some Epsom salt. These lakes resemble those in Wyoming very closely.

A company has been organized under the name The Soda Deposits (Ltd.), with its head office at Fusilier, district of Kerrubert, to work the deposit north of Fusilier.

A large quantity of sodium and magnesium sulphate, which appears in winter in the form of the mineral bloedite, has been reported in Maskakee Lake, district of Vonda, Saskatchewan. This deposit is being worked by Salts & Chemicals (Ltd.), whose western plant is at Dana, Saskatchewan.

MEXICO.

Deposits of mixed sulphates, carbonates, and chlorides of sodium and potassium, mostly sodium salts, have been reported from the province of Zacatecas, Mexico, and have been used locally for making soap but do not appear to be of any commercial value for their content of sodium sulphate.

SOUTH AMERICA.

Small deposits of sodium sulphate at the foot of the Andes have been worked for use in the glass industry of Argentina, but much salt cake is still imported.

AFRICA.

The soda lakes of Egypt have long been known as a source of crude natural soda. Their description, therefore, does not belong here, but some mention may be made of them on account of the fact that the soda may have originated from sodium sulphate

through the action of organisms. This is the view of Sickenberger,³⁵ who visited them in 1892. This occurrence and that of the Pretoria salt pan ³⁴ are almost the only known natural deposits of soda free from sulphates.

These lakes lie in an almost rainless desert in a valley somewhat below sea level about 36 miles from the Nile and 60 miles from the Mediterranean. The edges of the valley are formed of rounded sand hills. Gypsum and salt are prominent associates of the trona. Sickenberger found that the springs supplying the lakes are of neutral reaction but carry sodium chloride and sulphate. Green algae abound in the basins near the springs and turn first to a currant-red, then to a brown as they gradually die, meanwhile, however, reducing the sulphates to sulphides. The brown mud formed by their remains is finally colored black by ferrous sulphide. This mud covers the bottoms of the lakes under the salt and soda and contains a micrococcus that causes the formation of carbon dioxide from the dead algae. In this way, apparently, the carbon dioxide of the atmosphere indirectly causes the change of sodium sulphate into sodium carbonate while hydrogen sulphide escapes.

Sodium sulphate has also been reported in the Katuree salt lake, north of Albert Nyanza.

ASIA.

Several lakes in Asia, like the sodium sulphate lakes in Wyoming, Utah, and western Canada, deposit Glauber's salt in cold weather. Among these may be mentioned certain small lakes on the steppes in the neighborhood of Minussinsk and Abakansk, in southern Yeniseisk, described by Ludwig, ³⁵ especially Lakes Altai, Beisk, and Domoshakovo, which are underlain by solid Glauber's salt.

Schmidt ³⁶ reports a "soda lake" near Omsk fairly rich in sodium sulphate.

The Kara Bugas Gulf, on the east side of the Caspian Sea, deposits Glauber's salt in winter which does not wholly redissolve in summer. In this way a very large permanent deposit of Glauber's salt has been formed. Ochsenius estimated the present annual increment at 1 centimeter.

A recent list of mines, wells, etc., in Armenia mentions one mine of Glauber's salt. This may be a lake mentioned by Alberti ³⁷ as lying in the Araxes Plain, southeast of Little Ararat.

³³ Chem. Zeitung, 1892, pp. 1645, 1691.

³⁴ Walker, P. A., The Pretoria salt pan, a soda caldera: South Africa Geol. Survey Mem. 20, p. 104, 1922.

³⁵ Ludwig, F., Chemische Untersuchung einiger Mineral-Seen ostsibirischer Steppen; Zeitschr. prakt. Geologie, vol. 11, p. 401, 1903.

³⁰ Schmidt, C., Hydrologische Untersuchungen: Acad. St.-Pétersbourg Mém., vol. 20, No. 4, p. 22, 1873.

⁸⁷ Halurgische Geologie, vol. 1, p. 73, Stuttgart, 1852.

Travelers have also noted the occurrence of Glauber's salt in certain other regions, such as the desert of Gobi and the Kirghiz steppe.

EUROPE.

Italy.—According to consular reports a company in Catania, Italy, capitalized at 1,000,000 lire, is engaged in producing natural sodium sulphate from mines in the territory of Montedoro, province of Girgenti.

Rumania.—Lacu Sarat, Rumania, is reported to deposit Glauber's salt in winter, like the Great Salt Lake.

Spain.—Thenardite has been noted at small lakes in Toledo, Spain, near Espartinas and Villamanrique.

According to a recent report ³⁸ crude sodium sulphate which carries a very large percentage of calcium sulphate and a little magnesium sulphate is worked at a profit at Miranda de Ebro, Province of Alava, Spain. The ore, which is mined at Cerezo de Rio Tiron, Province of Burgos, is transported to the factory by motor truck, where it is subjected to a leaching, evaporating, and crystallizing process that yields 97 per cent sodium sulphate. About 800 tons was made in 1921, but the projected capacity of the plant is 30,000 tons a year. The product is consumed in local glass factories.

Russia.—Glauber's salt is found in some of the saline lakes of Astrakhan. Its production from natural sources has been reported from Kuban, north of the Caucasus Range, and from Tiflis.

SULPHATE PROCESS OF MAKING WOOD PULP.

The sulphate process of reducing wood to pulp is so named because it involves the use of sodium sulphate, but this substance is used only in making the sodium sulphide that is one of the active chemicals in the process, the other being sodium hydroxide. The process might more properly be called the sulphide process. It is used in treating all the long-fibered woods. The pulp is generally not bleached but is mixed with varying proportions of mechanical pulp to form several varieties of kraft paper, a strong, tough paper used for wrapping paper and in making paper bags. As a matter of fact, however, sulphate pulp can be more easily bleached than soda pulp. The cost of labor in the sulphate process is slightly higher than in the soda process, on account of the smelting operation; on the other hand, the raw material is cheaper. Salt cake for this process should be ground and should contain at least 95 per cent of anhydrous sodium sulphate. The content of sodium chloride should not exceed 2 per cent.

⁸⁸ Rev. min., met. y de ing., No. 2863, p. 13, Jan. 8, 1923.

The process of cooking the fiber (see Fig. 13) is very similar to the so-called soda process, but the active material is in part sodium sulphide, formed by reduction of the sodium sulphate by coal, sawdust, and carbonaceous matter recovered from the waste liquors. These waste liquors contain carbonaceous matter, some sodium sulphate, and sodium carbonate; they are evaporated, first in multiple-effect or disk evaporators and then in rotary furnaces; and finally the residue is heated to fusion with the requisite quantity of fresh sodium sulphate and wood or coal. The product is dissolved in water and causticized with lime, yielding a solution of sodium hydroxide and

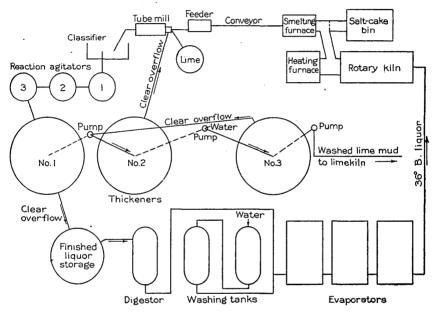


FIGURE 13.—Schematic outline of the sulphate process of making wood pulp.

sodium sulphide, which is suitable for acting on a fresh batch of wood fiber, after it is separated from the calcium carbonate sludge formed in causticizing. The highest efficiency in pulping is attained by the use of definite proportions of caustic to sulphide for each kind of wood.³⁹

The Dorr Co., 101 Park Avenue, New York, has perfected several devices that are useful in this process, including agitators, classifiers, and thickeners. Most of this company's machines are intended for continuous operation.

Some plants omit the multiple-effect evaporators; others have also perfected the recovery of certain by-products such as methyl alcohol,

⁵⁹ Textor, C. K., Alkali recovery in the sulphate process: Paper Trade Jour., No. 18, 1920.

oil of turpentine, and resins. Some engineering details of the process are discussed by H. K. Moore.⁴⁰

Reported estimates of the quantity of salt cake required per ton of pulp range from 280 to 700 pounds. According to information privately communicated to the writer by A. W. G. Wilson, of the Department of Mines, Ottawa, Canada, the capacity of plants in the United States using the process is about 160,000 tons of pulp annually, compared with 180,000 tons for Canadian plants, 50,000 tons for plants in Norway, and 150,000 tons for plants in Sweden. The calculated quantities of salt cake required for the plants in the United States range from 22,000 to 56,000 tons. Consular reports in January, 1923, state that Sweden is still in need of steady supplies of sodium sulphate, and that German exports were only 47,000 tons annually, compared with 83,000 tons in 1913.

The wood-pulp industry of the country is largely restricted to New England and the States about the Great Lakes, owing to the fact that the forests of these regions contain the varieties of timber best adapted to paper making, but some progress has also been made in using southern pine.

In 1917 spruce supplied 55 per cent of the pulp made, and hemlock, balsam, and poplar most of the remainder. The Census Bureau and the American Paper & Pulp Association reported 3,822,000 tons of pulp, valued at \$275,900,000, produced in the United States in 1920. The consumption has increased enormously in recent years, so that the United States has passed from an exporting to an importing country. Unless some other fiber is found for use in paper making it will apparently be necessary in the next decade or so to develop the industry in the far West or in Alaska.

The following list of manufacturers of wood pulp who use sodium sulphate in the sulphate process of cooking wood has been compiled from such information as is available. This list is believed to be fairly compete for the United States, but many wood-pulp plants are also located in Canada.

Atlantic Pulp & Paper Corporation, Savannah, Ga. Bogalusa Paper Co., Bogalusa, La. Brown Co., Berlin, N. H. Central Paper Co., Muskegon, Mich. E-Z Opener Bag Co., Braithwaite, La. P. H. Glatfelter Co., Spring Grove, Pa. Nekoosa-Edwards Paper Co., Port Edwards, Wis. New York & Pennsylvania Co., Johnsonburg, Pa. Pyne Tree Paper Co., Gordon, Ga. J. & J. Rogers Co., Au Sable Forks, N. Y.

⁴⁰ Met. and Chem. Eng., vol. 17, p. 117, 1917.

Southern Paper Co., Moss Point, Miss. Stevens Point Pulp & Paper Co., Stevens Point, Wis. Wausau Sulphate Fibre Co., Mcsinee, Wis. West Virginia Pulp & Paper Co., 200 Fifth Avenue, New York City.

SODIUM SULPHIDE.

A small amount of sodium sulphide is made in the United States as a by-product of the barium industry, but most of that produced in this country is made by reducing sodium sulphate with coal. The chemistry of this process is similar to that in the manufacture of wood pulp, described above, the chief difference being that the carbon is supplied as coal instead of as char from carbonaceous residues. The production of all grades of sodium sulphide reported to the United States Geological Survey for the year 1920 amounted to 43,000 short tons, valued at \$2,962,000.

USE OF SODIUM SULPHATE IN GLASS MAKING.

In making glass the several ingredients, such as sand, soda ash, salt cake, coke, and niter, are weighed out in the proper proportions, mixed in mixing machines, and transferred to the pots in furnaces heated by gas. Several successive additions are made as the gaseous products escape. These products include sulphur dioxide when salt cake is used. The melt is eventually heated sufficiently to remove the bubbles of gas in it and then made into the intended articles.

Sodium sulphate is used in making bottle, sheet, and plate glass in order to provide the necessary alkali base and because it is cheaper than soda ash, which is the standard source of alkali. The disadvantages connected with the use of salt cake are that a reducing agent in the form of coke, charcoal, or coal must be added to the ingredients, the exact amount of which must be carefully regulated; that some sulphur compounds are very likely to persist in the glass; that salt cake usually carries some sodium chloride, sulphuric acid, or insoluble particles; and that the ground material tends to cake again on standing. Glassmakers desire salt cake with less than 1 per cent of either sodium chloride or sulphuric acid, less than 0.4 per cent of iron and aluminum oxide, less than 0.5 per cent of matter insoluble in water, and less than 0.2 per cent of magnesium sulphate.

PROSPECTING PERMITS AND MINING LEASES.

The act of Congress approved February 25, 1920, entitled "An act to promote the mining of coal, phosphate, oil, oil shale, gas, and sodium on the public domain" (public No. 146), authorizes the Secretary of the Interior to issue permits to prospect for sodium

compounds and leases for the production of them. The part of this act pertaining to sodium compounds is as follows:

SODIUM.

SEC. 23. That the Secretary of the Interior is hereby authorized and directed, under such rules and regulations as he may prescribe, to grant to any qualified applicant a prospecting permit which shall give the exclusive right to prospect for chlorides, sulphates, carbonates, borates, silicates, or nitrates of sodium dissolved in and soluble in water, and accumulated by concentration, in lands belonging to the United States for a period of not exceeding two years: Provided, That the area to be included in such a permit shall be not exceeding two thousand five hundred and sixty acres of land in reasonably compact form: Provided further, That the provisions of this section shall not apply to lands in San Bernardino County, California.

SEC. 24. That upon showing to the satisfaction of the Secretary of the Interior that valuable deposits of one of the substances enumerated in section 23 hereof has been discovered by the permittee within the area covered by his permit and that such land is chiefly valuable therefor the permittee shall be entitled to a lease for one-half of the land embraced in the prospecting permit, at a royalty of not less than one-eighth of the amount or value of the production, to be taken and described by legal subdivisions of the public-land surveys, or if the land be not surveyed by survey executed at the cost of the permittee in accordance with the rules and regulations to be prescribed by the Secretary of the Interior. The permittee shall also have the preference right to lease the remainder of the lands embraced within the limits of his permit at a royalty of not less than one-eighth of the amount of value of the production to be fixed by the Secretary of the Interior. Lands known to contain such valuable deposits as are enumerated in section 23 hereof and not covered by permits or leases, except such lands as are situated in said county of San Bernardino, shall be held subject to lease and may be leased by the Secretary of the Interior through advertisement, competitive bidding, or such other methods as he may by general regulations adopt, and in such areas as he shall fix, not exceeding two thousand five hundred and sixty acres; all leases to be conditioned upon the payment by the lessee of such royalty of not less than one-eighth of the amount or value of the production as may be fixed in the lease and the payment in advance of a rental of 50 cents per acre for the first calendar year or fraction thereof and \$1 per acre per annum thereafter during the continuance of the lease, the rental paid for any one year to be credited on the royalty for that year. Leases may be for indeterminate periods, subject to readjustment at the end of each twenty-year period, upon such conditions not inconsistent herewith as may be incorporated in each lease or prescribed in general regulation theretofore issued by the Secretary of the Interior, including covenants relative to mining methods, waste, period of preliminary development, and minimum production, and a lessee under this section may be lessee of the remaining lands in his permit.

Sec. 25. That in addition to areas of such mineral land which may be included in any such prospecting permits or leases, the Secretary of the Interior, in his discretion, may grant to a permittee or lessee of lands containing sodium deposits, and subject to the payment of an annual rental of not less than 25 cents per acre, the exclusive right to use, during the life of the permit or lease, a tract of unoccupied nonmineral public land, not exceeding forty acres in area, for camp sites, refining works, and other purposes connected with and necessary to the proper development and use of the deposits covered by the permit or lease.

Leases under this act give the lessee exclusive rights to mine and remove all minerals in the tracts involved for a period of 20 years and are then subject to renewal on such terms as the Government may determine. The lessee is required to expend a certain sum in development, to furnish a bond for \$10,000 and later one for \$5,000, and to pay the royalty and rental specified, besides paying taxes and furnishing monthly statements of output and annual reports with plats of buildings, development work, and related information.

Regulations concerning the permits to prospect, authorized by the above act, are given in Circular 699 of the General Land Office, from which the following directions are quoted:

Applications for permits should be filed in the proper district land office, addressed to the Commissioner of the General Land Office, and after due notation promptly forwarded for his consideration. No specific form of application is required, but it should cover, in substance, the following points, namely:

- (a) Applicant's name and address.
- (b) Proof of citizenship of applicant; by affidavit of such fact, if native born; or, if naturalized, by the certificate thereof or affidavit as to time and place when issued; if a corporation, by certified copy of the articles thereof.
- (c) Description of land for which the permit is desired, by legal subdivisions, if surveyed, and by metes and bounds, if unsurveyed, in which latter case, if deemed necessary, a survey sufficient more fully to identify and segregate the land may be required before the permit is granted; also a statement whether the land is vacant and unclaimed.
- (d) Reasons why the land is believed to offer a favorable field for prospecting.
- (e) Proposed method of conducting exploratory operations, amount of capital available for such operations, and the diligence with which such explorations will be prosecuted.
- (f) Statement of the applicant's experience in operations of this nature, together with references as to his character, reputation, and business standing. On the receipt of the application, if found in compliance with the terms of the act, a permit will issue and the district land officers be promptly notified thereof.

The form of permit issued under this act will be in substance as follows:

SODIUM PROSPECTING PERMIT.

THE UNITED STATES OF AMERICA,

Department of the Interior.

Know all men by these presents, that the Secretary of the Interior, under and by virtue of the act of Congress entitled "An act to promote the mining of coal, phosphate, oil, oil shale, gas, and sodium on the public domain," approved February 25, 1920, has granted and does hereby grant a permit to _______ of the exclusive right for a period of two years from date hereof to prospect the following described lands ______ for chlorides, sulphates, carbonates, borates, silicates, or nitrates of sodium, dissolved in and soluble in water, and accumulated by concentration, but for no other purpose, upon the express conditions as follows, to wit:

1. To begin the prospecting for said minerals within ninety days from date hereof and to diligently prosecute the exploration and experimental work during the period of such permit, in the manner and extent as follows, to wit:

- 2. To remove from said premises only such material as may be necessary to experimental work and the demonstration of the existence of such deposits in commercial quantities.
- 3. To afford all facility for inspection of such exploratory work on behalf of the Secretary of the Interior, and to report fully when required all matters pertaining to the character, progress, and results of such exploratory work, and to that end to keep and maintain such accounts, logs, or other records as the Secretary of the Interior may require.
- 4. Not to assign or transfer the permit granted hereby without the express consent in writing of the Secretary of the Interior.

Expressly reserving to the Secretary of the Interior the right to permit for joint or several use such easements or right of way upon, through, or in the lands covered hereby as may be necessary or appropriate to the working of the same, or of other lands containing the deposits described in said act; and further reserving the right and authority to cancel this instrument for failure of the permittee or licensee to exercise due diligence in the execution of the prospecting work in accordance with the terms hereof.

Valid existing rights, acquired prior hereto, on the lands described herein will not be affected hereby.

In witness whereof I have affixed my signature hereto and the seal of the Department this _____ day of ______, 19__.

Secretary of the Interior.

The same circular also gives the regulations regarding leases. Leases are authorized for areas not exceeding 2,560 acres that are shown to contain sodium compounds of commercial value. An application for a lease when filed with the district land office will be given a serial number and transmitted to the Commissioner of the General Land Office. When an application is filed in the district office notice thereof should be published in a newspaper, and proof of publication is required before action will be taken on the application. The following form is suggested.

The other regulations concerning applications, leases, permits for camp sites and refining works are given in full in Circular 699 of the General Land Office, which should be consulted for details.

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INDEX.

1	Page.	Page.
Abakansk, Siberia, deposits near	32	Dona Ana County, N. Mex., deposit in 24-26
Africa, deposits in	31-32	deposit in, map showing
Albany County, Wyo., deposits in	30	Downey Lakes, Wyo., deposits at 28-29
Allen, O. D., analyses by		Egypt, soda lakes of
Altai Lake, Siberia, deposits of	32	Equilibrium diagrams of certain salts at
Analyses of waters of saline lakes	20	different temperatures 8, 9, 10, 11, 12
Aphthitalite, mineralogy of	3	Espartinas, Spain, deposits near
Araxes Plain, Armenia, deposit in	32	Europe, deposits in
Arizona, deposits in	18-19	Freight rates on sodium sulphate
Armenia, deposit in	32	Fremont County, Wyo., deposit in 30
Asia, deposits in		Fry, Wyo., deposits near
Astrakhan, Russia, deposits near	33	Fusilier, Saskatchewan, deposit near 31
Bear Creek, Colo., deposits near	21	General Land Office Circular 699, extracts
Beisk Lake, Siberia, deposits of	32	from
Bertram, Calif., deposit near	19	Germany, exports of salt cake from
Big Lake, Wyo., analysis of water of	20	Gill Lakes, Wyo., deposits at
Big Sandy Creek, Wyo., deposit near	30	Glass making, use of sodium sulphate in 31, 33, 36
Big Smoky Valley, Nev., deposit in	24	Glauberite, crystal form of, figure showing 4
	22	mineralogy of
Black Rock Desert, Nev., deposits in	3-4	Glauber's salt, firms producing
Bloedite, mineralogy of		production of
Bonneville, Lake, Utah, deposits of	28	
Bothwell saline deposits, Wyo		uses of
Browns Station, Nev., deposit at		· · · · -
deposit at, analysis of	21	1 0, 1
Buckhorn Springs, Calif., deposit near	19	Granite Mountain, Nev., deposits from springs near 23
Buena Vista Valley, Nev., deposits in		2 0
deposits in, analysis of	22 22	Grant County, Wash., deposit in
Buffalo Peak, Nev., deposits near		
Burdsalls Soda Lakes, Colo., deposits at	21	Hanksite, crystal forms of, figure
California, deposits in		showing
Canada, deposits in	31	mineralogy of 4-5 Hardin City, Nev., salts at, analysis of 24
wood pulp manufactured in	35	, , , , , , , , , , , , , , , , , , , ,
Carbon County, Wyo., deposits in		
Carrizo Plain, Calif., deposit in	19	,,,
Casper, Wyo., deposits near	29	——————————————————————————————————————
Cerezo de Rio Tiron, Spain, deposit at	33 20	
Chatard, T. M., analysis by		
China, deposits in	33 18	Hot Springs County, Wyo., deposits in 30 Humboldt Lake, Nev., deposit near, analysis
Clarkdale, Ariz., deposit near	21	of
Claytonia claims, Idaho, deposits on	29	Humboldt Range, Nev., deposits near 22
Cody, Wyo., deposits near	21	Hydrochloric acid, manufacture of
Colorado, deposits in	1	Idaho, deposits in
• • • • • • • • • • • • • • • • • • •	2-5	Imperial County, Calif., deposits in
Compounds of sodium sulphate, mineralogy of	20	Independence deposits, Wyo
Daudt, H. W., analysis by	1	Italy, deposits in
Demand for sodium sulphate	21	Jefferson County, Colo., deposits in
Denver, Colo., deposits near Deposits of sodium sulphate, location of	1	Jones, J. D., sample collected by
		Jump Creek, Idaho, deposits near
origin of	20	Kara Bugas Gulf, Siberia, deposits of 32
	29-30	Katuree salt lake, Africa, deposits in
Devils Lake, N. Dak., analysis of water of	20	Kern County, Calif., deposit in
Dixie Valley, Nev., salt obtained by borings	20	Kirghiz Steppe, Siberia, deposits in
	23	Kuban, Russia, deposit near
Domoshakaya Laka Siharia danasits of	32	Laguna Salina, N. Mex. deposit at

INDEX.

I	Page.		Page.
Lahontan, Lake, Nev., alkali flats of	22	Public lands containing sodium deposits, law	
Laramie, Wyo., deposits near	28,30	pertaining to	
Law governing prospecting for and mining of		regulations governing prospecting on and	
sodium compounds	36-37	leasing of	
Leases for public lands containing sodium		Publications of Geological Survey relating to	
deposits, law pertaining to		sodium sulphate	40
regulations governing	38-40	Ragtown, Nev., deposits near	
Lyon County, Nev., deposit in	24	Rochester mining district, Nev., alkali flat	
McKittrick, Calif., deposit near	19	near	22
Malott, Wash., deposits near	28	Rumania, deposit in	33
Maskakee Lake, Saskatchewan, deposit in	31	Russia, deposits in	33
Mason Valley, Nev., deposit in	24	Saline lakes, analyses of waters of	20
Mexico, deposits in	31	Salt cake, firms producing	14-15
Mina, Nev., deposit near	23	manufacture of	13
Mineralogy of compounds of sodium sul-		prices of	13-14
phate	2-5	prices of, diagram showing range of	14
Minerals containing sodium sulphate	1	quantity marketed in United States	14
Mining leases for public lands containing		uses of	1
sodium deposits, law pertaining		Salton Sea, Calif., deposit near	19
to	36-37	San Andres Mountains, N. Mex., deposit near.	24
regulations governing	38-40	San Luis Obispo County, Calif., deposits in	19
Minussinsk, Siberia, deposits near	32	Santa Catalina, Ariz., deposit at	18
Mirabilite, crystal form of, figure showing	2	Sarat Lake, Rumania, deposits of	33
mineralogy of	2	Saturated solutions of certain salts, composi-	
Miranda de Ebro, Spain, deposit worked at	33	tion of, at different temperatures.	7-12
Mohave Desert, Calif., deposit in	19	Schaffer's Spring, Nev., sodium sulphate in	
Monahans, Tex., deposit near	27	water of	23
Mono Lake, Calif., sodium sulphate in 1	19-20	Schaller, W. T., analysis by	20
water of, analysis of	20	Searles Lake, Calif., salts in	20-21
Montedoro, Italy, deposits in	33	water of, analysis of	20
Munroe, Calif., deposit near	19	Sevier Lake, Utah, deposit in	27
Natrona County, Wyo., deposits in 2	29,30	Siberia, deposits in	32
Nevada, depsits in		Silver Peak, Nev., deposit near	24
New Mexico, deposits in 2		Smoke Creek Desert, Nev., deposits in	22, 23
Niter cake, composition of	16	salts from, analysis of	24
firms reporting sales of	16	Soap Lake, Wash., analysis of water of	20, 28
production of	16	Soda Lake, Calif., deposit in	19
= -	2, 16	Sodium, Wyo., deposits at	30-
North Dakota, deposits in	20	Sodium sulphate and potassium chloride, a	
Norway, wood pulp manufactured in	35	reciprocal salt pair	7-12
Nourse, M. R., assistance by	18	Sodium sulphide, quantity and value of out-	
Oban, Saskatchewan, deposit near	31	put of, in United States	36
Okanogan County, Wash, deposits in	28	Solubility of sodium sulphate	5-12
Omak Lake, Wash., salts in water of	28	figure showing curve of	5
Omsk, Siberia, deposit near	32	table showing.	6
Oregon, deposits in	26	Sou Hot Springs, Nev., deposits from	23
Osobb Valley, Nev., deposits from springs in.	23	South America, deposits in	31
Owens Lake, Calif., sulphates in	20	Spain, deposits in	33
water of, analysis of	20	Split Rock, Wyo., deposit near	30
Pacific Springs, Wyo., deposit near	30	Squaw Peak, Ariz., deposit near	18
Paper, sulphate process of making 3	3-36	Star Peak Range, Nev., deposits near	22
Park County, Wyo., deposit in	29	Steiger, George, analysis by	20
Pemberton, H., jr., and Tucker, G. P.,		Sucker Creek, Oreg., deposits near 21,	26-27
analysis by	20	Sulphate process of making wood pulp, de-	
Percy, Wyo., deposit near, analysis of	30	tails of	33-35
Permits to prospect for sodium deposits, law	.[Sweden, wood pulp manufactured in	35
pertaining to 3	6-37	Sweetwater River, Wyo., deposits in old	
regulations governing 3		channels of	29
Pima County, Ariz., deposits in	18	Texas, deposits in	27
Potassium chloride and sodium sulphate, a	[Thenardite, crystal forms of, figures showing.	3
	7-12	mineralogy of	2-3
Pretoria salt pan, South Africa, deposits at	32	Thermopolis, Wyo., sample from	30
Prospecting for sodium deposits, law per-	- 1	Thompson, D. G., material collected by	19⁴
taining to 36	6-37	Tiflis, Russia, deposit near	33
regulations governing permits for 38	8-40	Transition temperature of sodium sulphate	6-7

INDEX.

P	age.		Page.
Tucker, G. P., Pemberton, H., jr., and, analy-	-	Wilson, A. W. G., acknowledgment to	35
sis by	20	Wood pulp, manufacturers of, by sulphate)
Tulare Lake, Calif., salts in	21	process in the United States,	
water of, analysis of	20	list of	35-36
Tularosa Basin, N. Mex., deposits in	25	quantity and value of output in United	1
Turkey Creek, Colo., deposits near	21	States	. 35
Union Pacific Lakes, Wyo., salts in 3	0-31	sulphate process of making, details of	33-36
water of, analysis of	20	figure showing schematic outline of	. 34
Utah, deposits in	27	kinds of wood used in	35
Valmont, N. Mex., deposit near	24	salt cake required in, quantity of	. 35
Verde Valley, Ariz., deposit in	18	Wood-pulp industry, location of, in United	1
Villamanrique, Spain, deposits near	33	States	. 35
Wabuska, Nev., deposit near	24	Woodward, R. W., analysis by	21,30
Walker Lake, Nev., salts in water of	23	Wyoming, deposits in	28-31
Washington, deposits in	28	Yeniseisk, Siberia, deposits in	. 32
Wells, R. C., analysis by	20	Zacatecas, Mexico, deposits in	31
Wendover, Utah, denosit near	27	•	

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